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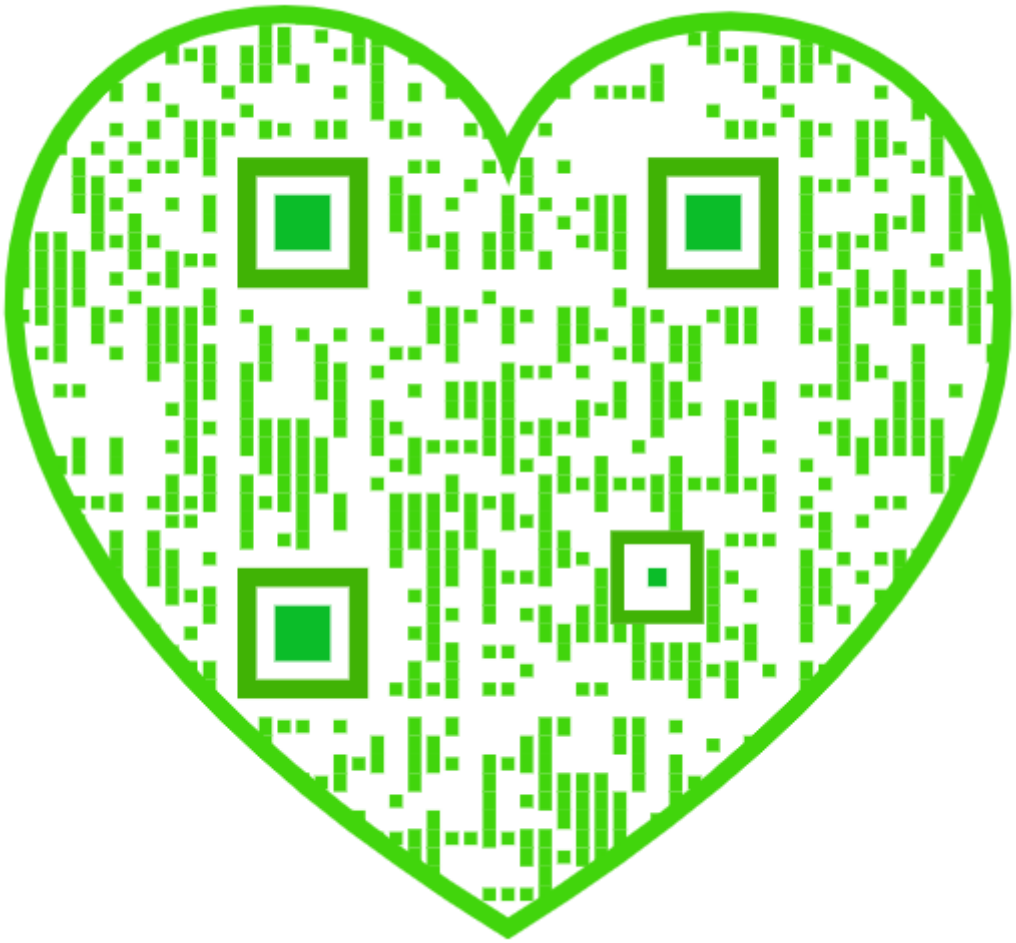

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# AN INTRODUCTORY COURSE OF LESSONS AND EXERCISES IN CHEMISTRY

(REWRITTEN 1919)

BY

E. P. SCHOCH, Ph. D.

Professor of Physical Chemistry,
The University of Texas.

Published by

THE CHEMICAL LABORATORY
OF THE UNIVERSITY OF TEXAS

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# PREFATORY NOTE.

This book aims to teach beginners the principles and facts which the chemist employes in his work, and the manner in which he solves his problems. It is thought that this manner of teaching the subject is more effective than the ordinary method of presenting descriptive chemistry.

The book includes the usual subject matter presented to beginners, but arranged so as to emphasize general principles and general facts. It presents the special properties of substances primarily as illustrations of the general facts and principles presented. One of the main features is the arranging of the subject matter with the view of presenting metathetical reactions thoroughly before presenting oxidation-reduction reactions. Another feature is the basing of the study of oxidation-reduction reactions on a thorough study of battery cells. The third main feature is a comparatively extensive and systematic presentation of organic chemistry. For a discussion of the pedagogic principles upon which this book has been developed, see Bulletin of the University of Texas, "Chemistry in the High School," Part III.

In this rewriting of the book, the chief object was to make it *self-contained:* no other text is required in connection with the lessons and exercises in this book.

However, it will be necessary for the student to secure other information in order to amplify and "round out" his knowledge of chemical facts. But the securing of such other information is an easier and more pleasant task than *the drilling* on fundamentals provided for in this text. For years the author has been of the opinion that there should be two distinct types of textbooks: one like this manual for drilling in fundamentals, and another for informational reading. This plan has been followed at the University of Texas with a fair degree of success for some years, and hence this text was rewritten and completed in accordance with this plan.

Professor William A. Felsing of the University of Texas has contributed many notes, and has helped extensively in rewriting the book, appreciation of which is gratefully acknowledged by the author.

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# AN INTRODUCTORY COURSE OF LESSONS AND EXPERIMENTS IN CHEMISTRY.

(Rewritten, 1919.)

## CHAPTER I.

## FUNDAMENTAL FACTS.

### 1. Introduction.

It is a matter of daily experience to see wood, coal, oil, candles, etc., disappear when they burn; iron changing to a red powdery substance when it rusts; gunpowder, when ignited, changing to gaseous substances. These and many other marked, permanent changes in the properties of substances are called chemical changes, and the study of such changes is the object of chemistry.

But there are many marked, permanent changes in substances which are not said to be chemical changes: ice changes to water at temperatures above its melting point and remains in the liquid form unless the temperature of its surroundings is lowered below the freezing point of water; a bar of steel may be magnetized and may then behave as a magnet for an indefinitely long period. The student naturally asks: what are some of the defining characteristics of *chemical* changes?

We can answer this question partly by presenting the chief defining characteristic of chemical changes; but, before doing this, we must present some facts which are fundamental to the whole subject.

### 2. Substances Exist in Only Three Different Forms—Solid, Liquid, and Gaseous.

Most of us are familiar with the fact that water exists not only in the liquid form, but also in the solid form as ice and in the gaseous form as aqueous vapor. However, we must realize that not only water, but *all other substances can exist in these three forms only: they exist in no other form.* The experiments given below will acquaint the student with the fact that this is true of two substances other than water. Furthermore, we must realize that any definite weight of a substance in any one of these forms will have the same weight when changed to either of the other two forms,—in other words, a change in form, as for instance from the solid to the liquid or to the gaseous form, will not entail a gain or loss of weight. This also is demonstrated in the experiments below.

The *Note Book.*—Since the student should begin at once to "write up" his experiments, a few directions concerning the manner of writing these notes will be in order here.

The notes should be written up periodically *shortly* after, but not *during,* the performance of an experiment.

The first thing needed in a note book is correct spelling, correct English, good penmanship and general neatness. Headings should be capitalized and underscored, the body of the "write-up" properly paragraphed, and the notes not crowded together.

All attempts to use blanks, to be filled in, or detailed "patterns," to be followed for the writing up of experiments, are to be avoided. A few general directions are naturally to be followed, but any approach to a "formula" to be used in writing up experiments should be decidedly avoided.

The experiments should not be numbered. The most important thing is to *devise for each experiment a heading* which states clearly the nature and object of the experiment. Considerable time should be spent in thought in order to devise headings that may be properly significant. A suitable heading is just as important as all the notes that follow.

In the body of the "write-up," the first thing to be given is a direct reference to the directions followed; but the directions themselves should *not* be copied into the note book. Then should follow a brief, definite statement of what was actually noted or observed which has not been given in the printed directions referred to.

The notes should always show the equations of the reactions in the experiment.

The frequent drawing of figures, particularly of such things as test tubes, burners, etc., is a waste of time. A figure should be drawn only if the apparatus is so elaborate that the figure is essential to accuracy and brevity of description; and when a figure is drawn it should be drawn carefully—in projection or plan rather than in perspective.

The following note on the experiment in Chapter II, Art. 2, may serve as an example of what is desired:

EXAMPLE OF NOTE BOOK ENTRY.

**THE PREPARATION AND COLLECTION OF OXYGEN AND THE DEMONSTRATION OF SOME OF ITS PROPERTIES.**

The experiment in Chapter II, Art. 2, Schoch's *Introductory Chemistry,* was performed as given.

It was observed that sulphur, carbon, phosphorus, and sodium, which had been heated to their kindling temperatures, burned vigorously in the oxygen gas. The product of the combustion of carbon is an invisible, inodorous gas (carbon dioxide); that of sulphur is an invisible gas with a suffocating odor (sulphur dioxide); that of phosphorus is a white solid (phosphorus pentoxide); that of sodium also is a white solid (sodium oxide).

Treated with water, the first three substances give solutions which turn blue litmus red, and the fourth gives a solution which turns red litmus blue. The formulae of the various chemical compounds and the quantitative relations in their formation are shown in the following equations:

$$C + O_2 = CO_2 \text{ (carbon dioxide), etc.}$$

**Incidental Experiment—Examination of Bunsen Burner.**

Examine a Bunsen burner. Take it entirely apart; then put it together again and light the gas.

Now turn the collar so that the air-holes are closed. The flame is yellow. Hold a piece of cardboard or a porcelain vessel in the flame; it becomes sooty.

Open the holes. The flame now should not be yellow anywhere, and should be from six to seven inches in length. Insert a piece of cardboard or a porcelain vessel: soot is not deposited now. Hold a match or a splinter of wood across the flame near the base: it will be burnt in two places, showing that there is an inner cooler region. Try inserting a match head into this cool region without lighting it.

The inner tube of the burner occasionally becomes closed up. It is opened by scraping it out with a knife-blade, care being taken not to open it so much that the amount of gas admitted is larger than can be rendered non-luminous by the amount of air admitted by the air-holes.

Cut off the supply of gas gradually by pinching the rubber tube. Suddenly the flame will shoot down and will be seen burning below. Release the rubber tube, and note the odor and the color of the flame; note also that the burner gets hot. To get the burner to burn correctly, the gas must be turned off and lighted again. When a small flame is needed, the air supply must be cut off in proportion to the gas.

**Experiment.**—(a) Secure a test-tube of the size ordinarily used; have it fairly clean but quite dry, and put into it as much powdered sulphur as will fill the tube about 1 cm., or one-half inch in length.

Have an instructor assign you to a fairly sensitive chemical balance, and learn how to use it. Note the number of the balance, and use only the same balance in any one experiment. With the aid of a loop of copper wire, suspend the filled test-tube from the balance pan hook, and ascertain the total weight of wire loop, test-tube, and sulphur. Make a temporary record of this weight on a piece of paper.

Light a Bunsen burner, and turn down the gas until the length of the flame does not exceed seven to eight centimeters (about three inches, since 1 inch equals 2.5 cm.). Grasp the test-tube near its open end with a holder, and put the lower, filled end into, or just above, the flame to heat the sulphur. Move the end of the test-tube to and fro slightly so that the flame may "lick" around the tube and heat all sides evenly. Allow the tube to be heated until the sulphur has melted and most of it distilled out of the bottom of the tube. Do not heat the tube farther than about 3 cm. from the closed end so as to avoid expelling any sulphur from the tube.

When through heating, hold the tube out of the flame to cool it for a few minutes, and then lay it aside on a dry towel until it is fairly cool. Then weigh the tube and contents on the same balance you used before, employing the same copper wire loop to suspend it.

If none of the contents were spilled mechanically, the tube and contents will be found to have the same weight as before, which shows that sulphur undergoes no change in weight while it is melted or vaporized.

Some one might object that we are weighting the sulphur in a solid state in both instances, and that it might have a different weight while hot and in the form of vapor. While this objection is a valid one, yet it should be pointed out that these various experiments performed by the student are merely for the purpose of indicating something of the correctness of a statement so as to predispose the student to accept the rest of the statement on faith. It is difficult to weigh a hot body, because the air currents started by a hot body tend to lift it and thus falsify the weight. However, having obtained the result above, the student is inclined to believe the further statement that even the hot vapor of the sulphur has the same weight as the solid sulphur.

(b) Repeat the above experiment with naphthalene. This substance is familiarly known as "moth balls."

Note that both of these substances change readily from one form to another, but that they exist in three different forms only; and that these changes in form do not entail changes in weight.

### 3. Even the Most Complex Changes in Matter Do Not Increase or Decrease the Weight of the Material Involved (Law of the Indestructibility of Matter).

Although it is easily seen and readily admitted by most of us that such simple changes as the melting of a substance or the evaporation of a liquid will not cause an increase or decrease in the amount (weight) of the material involved, yet we wish to have some further demonstration to convince us that matter will not gain or lose weight when subjected to changes which appear to be more extensive. For this purpose the experiments given below are here inserted. They show that, when substances undergo such marked changes as to produce new substances, even then the total weight of the material after the change is the same as it was before.

**Experiments.**—(a) *To be performed by the teacher only.* Secure a U-tube about 20 to 25 cm. (8 to 10 inches) in height, and 15 to 20 mm. in diameter, and fit one of the open ends with a two-hole rubber stopper. Secure two pieces of ordinary small glass tubing 15 cm. in length, and bend them at the mid-points to angles of about 45°, and "fire-polish" the ends. Secure two ordinary test-tubes, fit each with a one-hole stopper, and by means of the bent pieces of glass tubing, connect these through the two-hole rubber stopper with one opening of the U-tube. Put about 2 c.c. of concentrated ammonia solution into one test-tube, and about 2 c.c. of concentrated hydrochloric acid into the other. By means of a wire loop, suspend the whole apparatus on one arm of a large, delicate balance, and ascertain its weight. Then, grasp the U-tube near its open end, immerse it in some ice water, and warm both liquids simultaneously by means of two small flames. The heating should be moderate, and well regulated so that both liquids may boil at the same rate, and so slowly that none of the products are projected out of the open end of the U-tube.

Note the dense, white clouds and solid deposits of ammonium chloride formed. This substance is formed by direct chemical union of the hydrochloric acid gas with the ammonia gas.

Heat the liquids for about one minute at the longest. Then take the U-tube out of the water, dry it well, and weigh it again on the same balance. If nothing was expelled mechanically from the U-tube, the apparatus and contents will weigh just as much as before, which shows that any definite amount of matter has the same weight irrespective of any extensive chemical change which it may have undergone.

(b) Secure about 2 grams of lead in the form of thin sheets (or, less suitably, some tinfoil). Tear it into strips about 5 cm. in length and roll it with slight pressure into a ball, or wad, to drop it into an ordinary test-tube. Cover this ball with powdered sulphur, wipe the test-tube clean on the outside, and weigh it with its contents (suspending it on the balance pan hook by means of a loop of wire). Then grasp the test-tube at its upper end with a test-tube clamp, and heat the lower end of the test-tube fairly strongly until a *progressive* glow in the metal indicates that the sulphur is uniting with the metal! If this heating is done cautiously, nothing will be expelled mechanically from the test-tube, and the only changes in the contents will be due to the chemical union

of some of the sulphur with the metal. Hold the test-tube in the air for a while to cool, then lay it on a dry cloth until it is quite cool. Finally, weigh it again on the same balance with the same loop of wire with which it was previously weighed. It will be found to have undergone no change in weight.

Since weight is merely a measure of the quantities of substances or matter, the fact just stated shows that when substances undergo physical or chemical changes, the total amount of matter concerned does not change:—this general fact is known as the Law of the Indestructibility of Matter, and the value of knowing this fundamental law lies in the fact that by weighing, before and after a change, the various substances concerned in it, we find how much of each original substance has entered into the composition of the different resulting substances. In other words, the balance enables us to find out exactly what has happened during a change. Furthermore, the balance is the only generally applicable means with which this can be found out. While it is true that, in special instances, changes in the composition of substances can be noticed by means of one of our senses—sight, taste, feeling, etc., yet even then we do not perceive whether the change in composition is due to an *addition* of matter or to an *abstraction* of matter; but the balance reveals not only changes in the composition of matter, but it also tells us whether the change is due to an addition or an abstraction of one part of matter to or from another part. Therefore, the establishment of the Law of the Indestructibility of Matter made *weighing* the first unfailing and generally applicable means for ascertaining exactly what happens in chemical changes. Lavoisier was the first man who showed that matter is neither created nor destroyed by means of chemical changes (1774), hence he is called the founder of chemistry.

#### 4. The Fundamental or Defining Characteristic of Chemical Changes:—Law of Definite Proportion.

Let us compare two changes which in their outer aspects resemble each other, but only one of which is a chemical change, and let us point out the fundamental characteristic which distinguishes this chemical change from the other,—and hence from all other kinds of change. Let us take the decomposition of potassium chlorate at high temperatures—which is shown in the experiment below—and compare it with the drying of fruits or vegetables. In both cases, the solids lose weight—the potassium chlorate through the loss of oxygen, and the fruit through the loss of water—both of which escape as gases into the atmosphere. After the lapse of sufficient time, both changes cease, and the remnants will not lose any more weight. By dividing the total loss from each substance by the total amount of the substance taken, we obtain the loss per unit amount of each. Other por-

tions of potassium chlorate and of the same vegetable are then subjected to the same operation at the same or slightly different temperatures. The maximum loss experienced in these operations are again noted, and the losses per unit amounts are calculated.

The fundamental difference between these two changes lies in the fact that the loss of weight shown by any particular amount of potassium chlorate, such as one gram, is always exactly the same—namely, it is as near to 0.392 grams as the delicacy of the balance and the care taken in the operation makes possible. But the loss of weight shown by one gram of a potato on drying will vary from 0.65 grams to 0.85 grams, depending on the source and kind of potato; and, although the average loss is 0.75 grams, yet the result obtained with any potato will, in many cases, be different from this average result, even when the balance used is exceedingly delicate and the manipulation perfectly correct. We know the percentage of water in potatoes is never exactly the same, although it may be roughly the same. But the percentage of oxygen in potassium chlorate of all makes and from all sources is always the same—39.2 per cent—and this exact quantitative relation between the original and the resulting substances in a chemical reaction is the defining characteristic by means of which we distinguish between those changes which we call chemical from those which we designate as physical, etc.

The second experiment given below also illustrates this defining characteristic of chemical changes. It will be found that a definite weight of copper—say, 1 gram—will combine with as nearly 0.252 grams of sulphur as the method of operation renders possible.

**Experiment.**—Secure a small porcelain crucible (20 c.c.) and lid, a clay covered triangle, an iron ring-stand, and a Bunsen burner. Put the burner on the base of the ring-stand, clamp the 4-inch ring of the ring-stand in proper position for heating objects placed on the ring, put the clay covered triangle upon the ring, and the crucible on the triangle. Ascertain from an instructor whether or not you have arranged the apparatus correctly. Light the burner and warm the crucible and lid gently for a minute. Then allow them to cool, take them to a "quantitative" (or sensitive) balance, and ascertain their weight (instruction!). Fingers touching the crucible should clean and dry! Record the weight of crucible and lid on some convenient piece of paper. Then secure a small bottle of pure potassium chlorate, and with the aid of a small, clean porcelain spoon transfer about one gram of this substance to the crucible. Then weigh the crucible and lid again accurately. Record this weight and subtract the first weight from the latter to obtain the net weight of the potassium chlorate. Next place the crucible on the clay covered triangle again, and begin to warm it gently with a small non-luminous flame. Increase the flame so slowly that decrepitation is reduced to a minimum, but continue until the crucible is heated by the full strength of the burner flame. Turn out the flame, allow the crucible to cool, and weigh it again. Record this weight and subtract the first weight (above) to obtain the net weight of the residue. Divide the weight of the residue by the weight of the potassium chlorate taken, and record the result.

Wash the salt out of the crucible and lid, wipe them dry, warm them as at the beginning above, and weigh them again for the second part of this experiment.

Secure some pure, clean copper in the form of very thin sheets or turnings. If it is in the form of sheets, cut or tear it into strips of about $\frac{1}{2}$ cm. width and roll these loosely into balls. Put about 2 grams of copper into the dried, weighed crucible, and ascertain the exact additional weight due to the copper. Note this on a piece of paper. Then put into the crucible about 2 grams of powdered sulphur (weighing it approximately), put the crucible on a triangle on an iron stand to heat it. Begin heating the crucible with a small flame until the sulphur has melted, then increase the heat gradually until all the excess of sulphur has been driven off (i. e., when the sulphur vapors cease appearing):—stop heating promptly at this moment to avoid instituting a further change due to the action of the air upon the copper sulphide. Allow the crucible and contents to cool; then weigh it again carefully and note the weight on your piece of "note" paper. Subtract the weight of the crucible plus copper from the last weight, and divide the remainder by the weight of the copper:—the quotient should be nearly 0.252. Record the result as follows:

Ratio in which copper and sulphur combine to form copper sulphide, 1:0.252.

(Putting your own result in place of 0.252 here.)

This experiment may be carried out equally well with lead in place of copper, but the ratio in which lead and sulphur combine is naturally different from that in which copper and sulphur combine.

### 5. How Compounds Are Distinguished from Elements.

The experiments under Art. 4 show that the weight relation of potassium chlorate to its residue is such as to show that potassium chlorate consists of—is a compound of—the residue plus something else, and that the copper sulphide is a compound of copper and sulphur.

A similar but extensive search with the aid of the balance has revealed that certain substances are never compoundable from others, and these substances are known as *elements.*

### 6. Number and Kinds of Elements.

At present about eighty different elements are known. Among them are many familiar substances such as *sulphur,* carbon (e. g., lampblack and charcoal), *nitrogen* (which constitutes 79 per cent of the volume of the air), metals such as *iron, lead, zinc, copper,* and many others. The elements are roughly classed into *metals* and *non-metals.*

### 7. Mixtures and Compounds.

When substances are simply put together—i. e., mixed—they do not necessarily form compounds with each other. Frequently, they remain side by side, unchanged, and could remain so indefinitely. Naturally, mixtures have only those properties which their constituents show separately. Compounds, however, have

new properties distinct from those possessed by their components. Yet in many instances it is difficult to determine whether or not any particular aggregate is a mixture or a compound of the different substances in it, and the distinction can only be made with a wide knowledge of chemical facts.

**8. Derivation of the Atomic Weight Table.**

*A study of the weight relations between reacting elements reveals that we may find a set of numbers (one for each element), any two of which give either directly the ratio in which their corresponding elements combine by weight, or they give this ratio after they have been multiplied by only simple factors, such as 2, 3, 4, etc. (Law of the Existence of a Set of Single Relative Combining Weights).*

By direct trial chemists found out years ago that the different elements combine or react with each other in different ratios, but the *same* elements always combine or react in the *same* ratios *by weight.* Thus they found out that, by weight,

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| hydrogen | reacts | with | oxygen | in | the | ratio | 1:8 |
| " | " | " | sulphur | " | " | " | 1:16 |
| " | " | " | carbon | " | " | " | 1:3 |
| " | " | " | chlorine | " | " | " | 1.35.5 |
| " | " | " | calcium | " | " | " | 1:20 |
| " | " | " | copper | " | " | " | 1:31.8 |
| oxygen | " | " | sulphur | " | " | " | 1:1 |
| " | " | " | carbon | " | " | " | 1:.375 |
| " | " | " | chlorine | " | " | " | 1:1.109 |
| " | " | " | calcium | " | " | " | 1:2.5 |
| " | " | " | copper | " | " | " | 1:3.97 |
| sulphur | " | " | carbon | " | " | " | 1:.187 |
| " | " | " | chlorine | " | " | " | 1:1.11 |
| " | " | " | calcium | " | " | " | 1:1.25 |
| " | " | " | copper | " | " | " | 1:1.99 |
| carbon | " | " | chlorine | " | " | " | 1:11.83 |
| " | " | " | calcium | " | " | " | 1:1.666 |
| " | " | " | copper | " | " | " | 1:2.66 |

In order to record the weight relations in which all the different elements react to form the many thousands of compounds which exist, an almost interminable list would have to be made, and hence chemists have naturally tried for many years to simplify the manner of making these records. Of the many different schemes tried, only the following gave a useful result. The essential part of this scheme consists in selecting some one element (hydrogen) and calculating the weight of each of the other elements which is used up in *reacting* with unit amount of hydrogen *either by direct reaction,* or by reacting with as much of a third element as would itself react with unit amount of hydrogen. For the elements above which react *direct* with hydrogen, the first group of ratios give the numbers for this purpose. In order to

change the other ratios to fit this purpose, we proceed as follows: For example, to express the ratios by weight in which oxygen reacts with elements other than hydrogen, we take the corresponding ratios obtained from experiments, and recalculate them so that the amount of oxygen in all these ratios is 8,—that is, the amount of oxygen which reacts with 1 part of hydrogen. Recalculated in accordance with this idea, the experimental data above gives us—

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 8 | parts | of | oxygen | react | with | 8 | parts | of | sulphur |
| 8 | " | " | " | " | " | 3 | " | " | carbon |
| 8 | " | " | " | " | " | 8.875 | parts | of | chlorine |
| 8 | " | " | " | " | " | 20 | " | " | calcium |
| 8 | " | " | " | " | " | 31.8 | " | " | copper |

In order to do for sulphur what we did for hydrogen just now, we must use 16 parts sulphur in every ratio, because 16 parts sulphur react with 1 part hydrogen; hence the data above give, on recalculation, the following ratios by weight of sulphur reacting with other elements than oxygen:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 16 | parts | sulphur | react | with | 3 | parts | carbon |
| " | " | " | " | " | 17.76 | " | chlorine |
| " | " | " | " | " | 20 | " | calcium |
| " | " | " | " | " | 31.8 | " | copper |

In the same way we obtain the following figures for carbon:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 3 | parts | carbon | react | with | 35.5 | parts | chlorine |
| " | " | " | " | " | 5 | " | calcium |
| " | " | " | " | " | 7.99 | " | copper |

For convenient inspection, we will place these four sets of ratios into the following table, placing at the top of the first column the element hydrogen with the number 1, and below the elements which react with it, together with the relative amounts of their weights which are used up in reacting with 1 part hydrogen; then placing at the head of the second column the element oxygen with the number 8,—that is, the number of parts which combine with 1 part of hydrogen, which is the basal amount for the whole table, and this number for oxygen is to be placed in the same horizontal line in which it is placed in the first column. Then the elements with which oxygen reacts are placed in the second column on the same horizontal line in which they appear in the first column. In the same way we have arranged the third column for the compounds of sulphur with various elements with which it reacts, and the fourth column for the compounds of carbon with the various elements with which it reacts. Thus we obtained the following table:

PROPORTIONS BY WEIGHT IN WHICH CERTAIN ELEMENTS REACT, AND THE DERIVED REACTING WEIGHTS.

| Column I | Column II | Column III | Column IV | Column V |
|---|---|---|---|---|
| 1 part hydrogen with (below)— | | | | Reacting weights 1 for hydrogen |
| 8 parts oxygen | 8 parts oxygen with (below)— | | | 8 for oxygen |
| 16 parts sulphur | 8 parts sulphur | 16 parts sulphur with (below)— | | 8 for sulphur |
| 3 parts carbon | 3 parts carbon | 3 parts carbon | 3 parts carbon with (below)— | 3 for carbon |
| 35.5 parts chlorine | 8.875 parts chlorine | 17.75 parts chlorine | 35.5 parts chlorine | 8.875 for chlorine |
| 20 parts calcium | 20 parts calcium | 20 parts calcium | 5 parts calcium | 5 for calcium |
| 31.8 parts copper | 31.8 parts copper | 31.8 parts copper | 7.99 parts copper | 7.99 for copper |

Next let us glance along every horizontal line in this table, pick out the smallest number occurring in that line, and put it in column V on the same line. Thus we will obtain 1 for hydrogen, 8 for oxygen, 8 for sulphur, 3 for carbon, 8.875 for chlorine, 5 for calcium, and 7.99 for copper.

It is evident that the numbers for any one element in the first four columns, for instance, for sulphur, are *simple* multiples of these smallest numbers in column V. Furthermore, any ratio in which the elements react may be written by using the numbers in column V, *either directly* or after they have been *multiplied by only a simple factor*—2, 3, etc. Thus the ratio by weight in which hydrogen and oxygen combine is that of the two numbers in column V—1:8; and the same is true for sulphur and oxygen for which the ratio is 8:8; while the reacting ratio for oxygen and calcium, though not 8:5, is obtained by multiplying the 5 by 4, which gives the ratio 8:20. Similarly the combining ratio for chlorine and carbon, though not 8.875:3, is obtained by multiplying the number of chlorine in column V by 4, which gives the correct ratio 35.5:3.

What has here been illustrated with a few elements is true for all elements; and column V, if lengthened out to include all elements, gives a set of numbers, one for each element, which give, either at once, the ratio in which their corresponding elements combine by weight, or they give this ratio after they have been multiplied by *only simple factors*, such as 1, 2, or 3 (Law of the Existence of a Set of Single Relative Combining Weights.)

**9. The Atomic Structure of Matter.**

The two *laws* of combining weights pointed out in the foregoing are due to the fact that (1) each element is made up of small particles (atoms) of the same weight and alike in every other way, which do not subdivide during chemical changes and which have the power to attract, or to hold on to, other atoms; (2) that the atoms of different elements have different weights; and (3) when elements combine to form compounds, their atoms combine in groups of two or three or four, etc., which groups are called *molecules,* and a quantity of any definite substance is merely a collection of groups or molecules of a particular kind. It follows from the last statement that a compound must always contain its elements in *exactly* the same ratio by weight, and this accounts for the law of definite proportion.

To understand how the atomic structure accounts for the existence of a *Set of Single Relative Combining Weights,* let us assume that the numbers in column V are the *relative* weights of the atoms of the different elements. Thus, if a compound—e. g., carbon bisulphide—is made up of groups or molecules containing one atom of carbon combined with two atoms of sulphur, then the ratio by weight in which these elements combine would be obtained by multiplying by 2 the number for sulphur in column V, which is actually the case.

**10. Atomic Weights.**

The numbers in column V are not the same as those given in Tables of Atomic Weights, because, in drawing up this table above, we did not consider the *total amounts of each element in each molecule* of the different compounds. However, when the latter is done we obtain the real atomic weights, and this will now be shown. The total amount of matter in a molecure—that is, the molecule weight—can be determined (as shown in Chapter VI). Thus the molecular weight of the hydrogen-oxygen compound, *water,* is found to be 18 times as heavy as the weight of an hydrogen atom; and since, in this compound the ratio of hydrogen to oxygen is 1:8, the amount of hydrogen in this molecule must be one-ninth of 18, or 2; and the total amount of oxygen must be eight-ninths of 18, or 16. These results would seem to indicate there are either two atoms of hydrogen ($2\times1=2$), and also two atoms of oxygen ($2\times8=16$) in each molecule of water, or that either or both atoms are twice as large: to decide this question, we draw up a table similar to the preceding one, in so far as we place, in each horizontal line, the

amount of one particular element in different compounds, and we select the proper number for the atomic weight by considering that the least amount of any particular element found in the molecule of any one of its compounds is the amount corresponding to one atom.

| | | | | | | |
|---|---|---|---|---|---|---|
| Amount of Hydrogen in mol. of | Water 2 | Hyd. Sulphide 2 | Methane 4 | Hyd. Chloride 1 | | Least amount of Hydrogen in any mol. 1 |
| Amount of Oxygen in mol. of | Water 16 | Sulphurous acid 32 | Carbonic acid 32 | Chlorine dioxide 32 | Calc. oxide 16 | Least amount of Oxygen in any mol. 16 |
| Amount of Sulphur in mol. of | Sulphurous acid 32 | Hyd. Sulphide 32 | Carbon bisulphide 64 | Sulphur dichloride 32 | Calc. Sulphide 32 | Least amount of Sulphur in any mol. 32 |
| Amount of Carbon in mol. of | Methane 12 | Carb. bisulphide 12 | Carbonic acid 12 | Carbon Tetra-Cl. 12 | Calc. Carb. 24 | Least amount of Carbon in any mol. 12 |
| Amount of Chlorine in mol. of | Hyd. Chloride 35.5 | Sulphue dichloride 71 | Carbon Tetra-chloride 142.0 | Chlorine oxide 35.5 | Calc. Chloride 71 | Least amount of Chlorine in any mol. 35.5 |

Strictly speaking, the values of the atomic weights now employed are not exactly those given above—which were obtained with the weight of the hydrogen atom assumed equal to *one,* but they are values obtained with the weight of the hydrogen atom equal to 1.008 nearly, so chosen as to make the value of the weight of the oxygen atom *exactly* 16.

### 11. A Set of Symbols for Expressing Weight Relations in Compounds.

To represent the atoms and the atomic weights of elements, chemists use the initial letter of the name (English or Latin) of each element (sometimes coupled with an additional letter). The formula of a compound is expressed by writing, side by side, the symbols of all the elements in its molecules. Thus the formula for potassium chlorate is written thus—$KClO_3$—which means that its molecule contains one atom or 39 parts by weight of potassium, plus one atom or 35.5 parts by weight of chlorine, plus three atoms or $3\times16$ parts by weight of oxygen.

To express the weight relations for the change which potassium chlorate undergoes in the first experiment under Article 4, we write—$2KClO_3=2KCl+3O_2$, which means that two molecules of potassium chlorate in changing produce two molecules of the substance denoted by KCl (potassium chloride) and three molecules of oxygen (each of the latter being composed of two atoms). These symbols also state that the number of parts by weight expressed by $2KClO_3$, which is $2(39+35.5+48)$ or 245, yield as many parts by weight of potassium chloride as are expressed by

2KCl, which is 2(39+35.5) or 149, and as many parts by weight of oxygen as are expressed by $3O_2$, which is $3(16\times2)$ or 96.

### 12. Calculation of the Amounts of Substances Used in Practical Work.

With the above expression the amount of oxygen obtained from different amounts of potassium chlorate is readily calculated. Thus to find how much oxygen is obtained by heating 5 grams, proceed as follows:

Write down the *symbolic* expression (equation) for the relations of the weight obtained by experimenters,—$2KClO_3 = 2KCl + 3O_2$; underscore the symbols of the *two* substances with which the problem deals,—i. e., underscore $2KClO_3$ and $3O_2$. Put the "given weight" and "x" above the respective underscored symbols; and then put underneath these symbols the numbers which they designate,—thus

$$\underset{245}{\overset{5}{2KClO_3}} = 2KCl + \underset{96}{\overset{x}{3O_2}}$$

Next, put the four numbers (including x) into a proportion, reading each line in the same direction, say, from left to right,—thus

$$5 : x :: 245 : 96$$

Solving for x gives the answer,

$$x = \frac{5\times96}{245} = 1.96$$

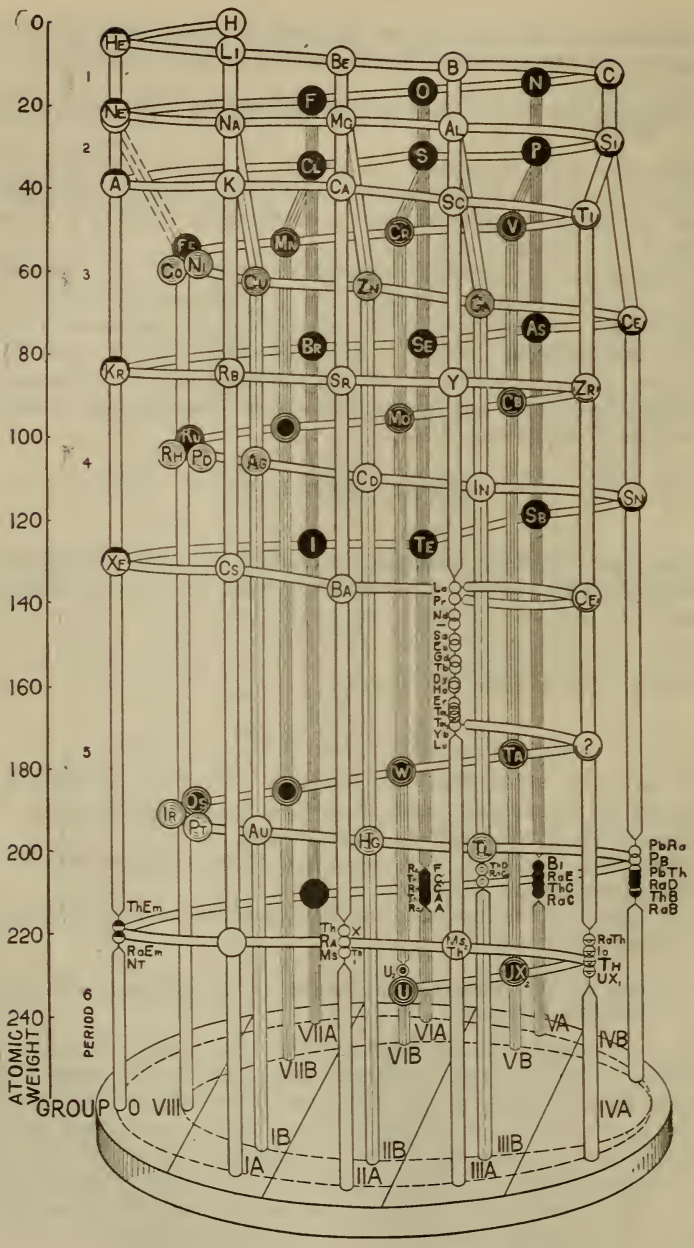
It is to be noted that the equation—$2KClO_3 = 2KCl + 3O_2$—gives more information than is needed in this calculation; the extra amount is naturally to be neglected.

*Problems:* Calculate how much potassium chlorate will give 5 grams of potassium chloride.

How much potassium chloride will be obtained when 10 grams of oxygen are obtained?

### 13. Table of the Elements Arranged in Accordance with Their Natural Relations.

If the names of the elements are arranged in the order of their "atomic numbers" (such numbers being obtained by certain frequency measurements of the X-ray radiations of the elements, see footnote I), which is generally also the order of their atomic weights, and if they are placed consecutively at equal intervals on a piece of tape and the tape wound on a suitable frame-work, as in the accompanying sketch, the vertical columns present the names of similar elements or of elements which are closely related in properties.




Harkin's Model of the Periodic System.

A simpler manner of printing the same arrangement is given in the table below. The first complete table of this kind was drawn up by the Russian chemist, Mendelejeff, and simultaneously but independently by the German chemist, Lothar Meyer, in 1869. It is known as the *Periodic System of the Elements,* because from one element to the next similar element all the intervening elements present a progression of properties which include all the different types, and which progression ends on the element similar to the initial element. Each set of elements showing such graduation of properties is known as a *period,* and the aggregate arrangement of the entire series of *"periods"* is known as the *Periodic System.* Stated briefly, the properties of the elements as well as the properties (see footnote 2) of their compounds form a *periodic* function or relation of the atomic numbers (or generally, atomic weights) of the elements.

*Exercise:* Commit to memory the elements in the first two short periods and in the first long period. Memorize them in their exact *order;* memorize their *symbols* and their approximate atomic weights.

*Footnote 1:* A very important and valuable method of determining the *atomic numbers* of elements was dicovered by H. G. T. Moseley. He made a thorough and systematic study of the characteristic X-ray radiations (the "K" radiation) of the elements, in which he found that the frequencies (f) of the radiations increase with increasing atomic weight of the element according to the simple relation

$$f=k(A^n-1)^2$$

where k is a constant and $A_n$ is the atomic number.

*Footnote 2:* Some of the properties referred to are malleability, ductility, melting points, specific gravity, coefficient of expansion, latent heat of fusion (physical properties) and similarity of compounds, and the gradual transition of *basic* properties of the compounds of the elements on the left to *acidic* properties of the compounds of the elements on the right in a period (chemical properties).

**Questions on Chapter I.**

1. With what general *experimental means* or operation are compounds distinguished from elements?
2. About how many elements are known? Mention a few elements that are commonly known. Into what two classes are elements divided? In general, what do the oxides of these two classes form on hydration?
3. Why is the union of sulphur with copper considered to be

## PERIODIC SYSTEM

| Type Comp. | | Group 0 | Group 1 | Group 2 | Group 3 | Group 4 | Group 5 | Group 6 | Group 7 | Group 8 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $ECl$, $E_2O$ | $ECl_2$, $EO$ | $ECl_3$, $E_2O_3$ | $EH_4$, $EO_2$ | $EH_3$, $E_2O_5$ | $EH_2$, $EO_3$ | $EH$, $E_2O_7$ | $EO_4$ |
| Valence | | 0 | +1 | +2 | +3 | −4, +4 | −3, +5 | −2, +6 | −1, +7 | +8 |
| PERIODS | 1 | He 4 | Li 9.1 | Gl 11 | B 12 | C 12 | N 14 | O 16 | F 19 | |
| | 2 | Ne 20.2 | Na 23 | Mg 24.3 | Al 27.11 | Si 28.3 | P 31 | S 32 | Cl 35.5 | |
| | 3a | A 39.9 | K 39.1 | Ca 40 | Sc 44 | Ti 48 | V 51 | Cr 52 | Mn 55 | Fe 55.8 Co 59 Ni 58.7 |
| | 3b | | Cu 63.6 | Zn 65.4 | Ga 70 | Ge 72.5 | As 75 | Se 79.2 | Br 80 | |
| | 4a | K 83 | Rb 85.4 | Sr 87.6 | Y 89 | Zr 90.6 | Cb 93.5 | Mo 96 | | Ru 101.7 Rh 103 Pd 106.7 |
| | 4b | | Ag 108 | Cd 1124 | In 115 | Sn 119 | Sb 120 | Te 127.5 | I 127 | |
| | 5a | Xe 130 | Cs 133 | Ba 137.4 | La 139 | Ce 140 | Nd 144.3 | Sa 150.4 | Eu 152 | |
| | 5b | | | | | | | | | |
| | 6a | | | | Yb 172 | | Ta 181.5 | W 184 | | Os 101.7 Ir 103 Pt 195.2 |
| | 6b | | Au 197 | Hg 200.6 | Tl 204 | Pb 207 | Bi 208 | | | |
| | | Nt 222.4 | | Ra 226.4 | | Th 232.4 | | U 238.5 | | |

The atomic weights are given in round numbers.

a *chemical* change, but the dissolving of sugar in water *not* a chemical change?

4. What is the most important use that chemical symbols serve?

5. State all the fundamental laws of matter set forth in this chapter. Who is the founder of systematic chemistry? State specifically what he did that earned him his title.

## CHAPTER II.

## THE INFLUENCE OF TEMPERATURE UPON CHEMICAL CHANGES. ILLUSTRATED MAINLY WITH EXPERIMENTS IN WHICH OXYGEN PLAYS THE CHIEF ROLE.

### 1. Introduction.

In the first chapter we presented some of the fundamental facts of chemistry without attempting to teach any special or individual properties of substances. In this chapter we shall begin the presentation of some special facts, a knowledge of which is essential to a knowledge of the subject.

### 2. The Separation of Oxygen Gas from Some of Its Compounds at High Temperatures.

Although most compounds of oxygen remain unchanged when heated to high temperatures, yet there are a notable number of them which liberate oxygen at high temperatures. These experiments given below serve to acquaint the student with a number of substances of which this is true.

The quantitative relations between the original and resulting substances as well as the compositions and names of the products occurring in the accompanying experiments are given below; commit these names, formulæ, and equations accurately to memory:

$$\underset{\text{lead peroxide}}{2PbO_2} = \underset{\text{lead oxide}}{2PbO} + \underset{\text{oxygen}}{O_2}$$

$$\underset{\text{potassium nitrate}}{2KNO_3} = \underset{\text{potassium nitrite}}{2KNO_2} + \underset{\text{oxygen}}{O_2}$$

$$\underset{\text{mercuric oxide}}{2HgO} = \underset{\text{mercury}}{2Hg} + \underset{\text{oxygen}}{O_2}$$

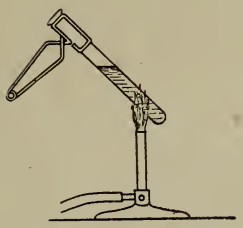
$$\underset{\text{manganese dioxide}}{3MnO_2} = \underset{\text{manganese oxide}}{Mn_3O_4} + \underset{\text{oxygen}}{O_2}$$

Make a proper note book entry concerning the following experiment, mentioning particularly the appearance of each residue.

**Experiment.**—Put a small amount of potassium chlorate into an ordinary dry test-tube and heat it in a Bunsen flame.

Note that the mass melts, and that bubbles of a gas escape from the molten mass. In order to ascertain something about the nature of this gas, lower a glowing splinter into the test-tube,—but not so low as to touch the molten mass (should the latter happen, hold the test-tube so that it will point straight up in the air until the action is over).

At the high temperature to which the potassium chlorate is heated, it gives us *oxygen*. The gas formed in the test-tube is more concentrated



Correct method of holding and heating a test-tube

than the oxygen in the atmosphere, and hence the splinter burns vigorously within the tube while, in the air, it glows merely.

In the same manner, try lead peroxide (or dioxide), potassium nitrate, mercuric oxide, manganese dioxide (the latter requires a higher temperature than the others and hence a hard glass test-tube must be used).

### 3. Catalytic Action.

**Experiment.**—Heat a small amount of potassium chlorate in a test-tube until it is barely melted, then sprinkle a little powdered manganese dioxide upon it.

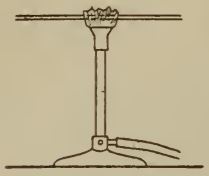
While performing the experiment above, note how much more rapidly the gas (oxygen) is evolved after the addition of the manganese dioxide than before. The change still consists of the decomposition of potassium chlorate while the manganese dioxide remains unchanged in the reaction. Since the tendency to change which is exerted by the potassium chlorate is likely to be the same here as before because the conditions are the same, and since the reaction takes place much more rapidly, it follows that the manganese dioxide must affect the ease or difficulty with which the change takes place. This effect may be aptly compared to the effect of adding oil to the bearings of a piece of machinery. The oil does not increase the driving force of the machinery, but it lessens the resistance and thus helps to increase the speed with which the same force drives the machinery. Substances which act like the manganese dioxide in this example are called "catalyzers."

### 4. The Preparation of Several Bottles Full of Oxygen Gas and the Combustion of Several Elements in it.

**Experiment.**—Secure a hard glass test-tube; fit it with a cork and a delivery tube as shown in the accompanying figure. For softening the cork, perforating it, and for bending the class tube, special directions will be given by the instructor. See also the figures below, which show how glass tubes are to be heated. Fill the test-tube half full with a

mixture composed of approximately two parts of potassium chlorate and one part manganese dioxide (powdered). Be careful to keep paper, pieces of cork, and other combustibles out of this mixture.

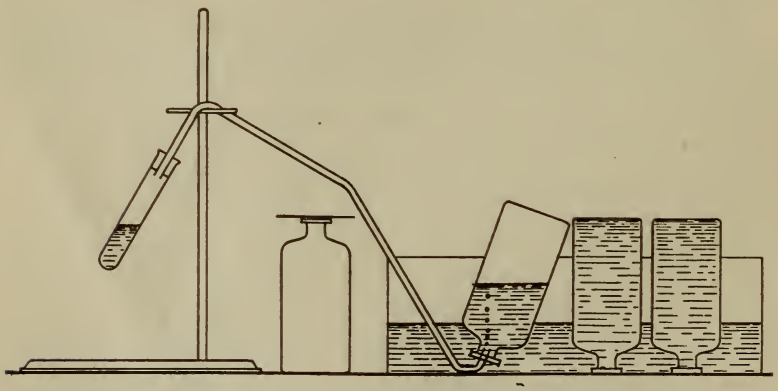
In the next operation, two students should work together. They should secure a water basin, four wide-mouth bottles, and four pieces of glass large enough to cover the mouths of the bottles. Assemble the whole as



Burner for Bending Glass Tubing

A Correctly Bent.
B & C Incorrectly Bent.

shown in the accompanying figure; heat the potassium chlorate and collect the gas. Secure a deflagrating spoon, put a small piece of charcoal in it, heat this in a burner flame, and lower it into one of the bottles, In this same way, proceed to burn sulphur in another bottle, phosphorus in a third, and a small piece of sodium in the fourth. Add a little distilled water to each of the bottles; shake the bottles with it so that the products of combustion may be absorbed by the water, and drop into



each of the first three bottles a piece of blue litmus paper, and into the fourth bottle a piece of red litmus paper. The instructor will show the burning of iron (picture cord) in oxygen. Record in your note book all observations made in connection with this experiment. What properties of oxygen gas—solubility, etc.—has this experiment revealed?

### 5. The Chemical Combining of Oxygen with Other Elements.

The above experiment introduced the student to a chemical change which is the reverse—in a sense—of the separation of

oxygen from substances,—namely, the combining of oxygen with substances. The substances burned combine with oxygen in definite relative amounts by weight. Thus 3 parts of carbon (charcoal) combine with 8 parts by weight of oxygen, and this is expressed by writing $CO_2$—which means 12 parts by weight of carbon to 32 parts by weight of oxygen, and hence the same as 3:8. The product of the combustion of phosphorus contains the elements in the ratio by weight of 31:40,—to express this we write $P_2O_5$. The relation of the weights for the compound formed by sulphur is expressed by the formula $SO_2$, that for sodium by the formula $Na_2O$ and that for iron by the formula $Fe_3O_4$.

Most elements combine with oxygen at high temperatures. With some elements this oxidation is accompanied with the evolution of little or no heat, and with others heat is absorbed. Some elements (e. g., mercury and platinum) do not combine with oxygen except at low temperatures—and then usually very slowly. Aside from the absolutely non-active elements which form no compounds whatever (helium, argon, crypton, neon, etc.), all the elements except fluorine form compounds with oxygen.

### 6. The Hydration of Oxides.

When, in the experiment under Article 4, the products of combustion are treated with water, the following reactions take place:

| | | | | |
|---|---|---|---|---|
| $CO_2$ | + | $H_2O$ | = | $H_2CO_3$ |
| Carbon dioxide | | Water | | Carbonic acid |
| $SO_2$ | + | $H_2O$ | = | $H_2SO_3$ |
| Sulphur dioxide | | Water | | Sulphurous acid |
| $P_2O_5$ | + | $3H_2O$ | = | $2H_3PO_4$ |
| Phosphorus pentoxide | | Water | | Phosphoric acid |
| $Na_2O$ | + | $H_2O$ | = | $2NaOH$ |
| Sodium oxide | | Water | | Sodium hydroxide |

Iron oxide does not react with water.

When substances react with water, as in the foregoing examples, they are said to become *hydrated*, and the reactions are known as *hydrations*.

The hydration of oxides of "non-metals" (e. g., carbon, sulphur, phosphorus) generally produces compounds known as acids, solutions of which have a sour taste, and turn blue litmus red. The hydration of oxides of metals (e. g., sodium) generally produces basic hydroxides, solutions of which turn red litmus blue.

The above facts, formulæ, and equations should be accurately impressed upon the memory.

Calculate how much water is required to hydrate five grams of each one of the oxides hydrated above.

### 7. Other Properties of Oxygen.

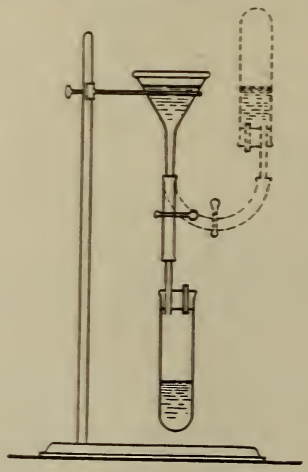
Besides the properties of oxygen learned through the experiments above, the following quantitative data concerning oxygen is desired sometimes, and hence it is here given for convenient reference. At 0° C. and under 1 atmosphere pressure pure oxygen gas dissolves in water with which it is in contact to the extent of approximately 4 volumes of the gas in 100 volumes of water. The solubility of gases is given by volume instead of by weight because the solubility of gas by volume is always the same irrespective of the extent to which it may be compressed by pressure. It follows, of course, that the solubility by weight is different with different pressures.

A liter of oxygen at 0° C. and under 1 atmosphere pressure weighs 1.429 grams. It is slightly heavier than air because four-fifths of the air is gas—nitrogen—which is seven-eighths as heavy as oxygen.

Oxygen becomes a liquid at —118° C. and a pressure of 50 atmospheres. With lower temperatures it liquefies, or remains liquid, under lesser pressures.

### 8. The Proportion by Volume of the Oxygen in the Air (After Cooley).

In order to determine the volume of oxygen in a gas, air for example, a solution of potassium pyrogallate is employed to ab-



sorb the oxygen. The decrease in volume is the volume of the oxygen in the gas.

**Experiment.**—Secure a large test-tube or any slender, cylindrical vessel of 60-80 c.c. capacity, and fit it with a two-hole rubber stopper. Into

one hole push a short glass nozzle, and into the other a well-fitting plug of glass rodding. Secure a glass funnel, rubber tube, and pinch clamp and fit up the apparatus as shown in the accompanying figure. Test the apparatus to ascertain that it is air-tight.

Secure 3 c.c. of a solution of pyrogallic acid, and 22 c.c. of a solution of potassium hydroxide, both of which have been prepared specially for this purpose, as follows: the first by dissolving 10 grams of pyrogallic acid in 30 c.c. of water, and the second by dissolving 240 grams of potassium hydroxide in 160 c.c. of water. (This will furnish enough for about ten experiments.)

When ready to perform the experiment, mix the two solutions, pour the mixture into the funnel, and while the test-tube is removed, fill the rubber tube and nozzle with the liquid; then, while the second hole of the rubber stopper is open, fit the stopper into the test-tube; finally, close the second hole of the stopper with the plug.

Without touching the test-tube except at the rubber stopper, open the pinch clamp: as soon as a few drops have entered the test-tube, they will absorb oxygen, and then the rest of the solution will flow in more rapidly. Close the clamp and invert the test-tube several times in order to bring the liquid thoroughly in contact with the enclosed air. Finally invert the test-tube, open the clamp and bring the level of the liquid in the test-tube on a level with the liquid in the funnel; then close the clamp again, put the test-tube upright, and mark with paper labels or rubber rings the position of (1) the surface of the liquid in the test-tube and (2) the bottom of the stopper.

Remove the test-tube and rinse it out with tap water. Then secure a burette, fill it with water, and with this ascertain the original volume of air in the test-tube and the volume of liquid which was drawn into the test-tube to fill the volume of the absorbed oxygen. Calculate what per cent, by volume, of the air is oxygen.

### 9. The Determination of the Solubility of Air in Water.

Half fill a 1-liter bottle with distilled water, cork, and shake vigorously until the water is saturated with air. Take the temperature of the water and also the barometric reading. Fit a small flask (100 c.c.) with a one-hole cork and delivery tube. The tube should not extend beyond the inner surface of the cork. Completely fill the whole apparatus, including the delivery tube, with the prepared water. Heat this to boiling and collect the gas in a small test-tube inverted into water. When no more gas comes over, equalize the levels of the water in the tube and trough and mark the level in the tube with a thin rubber ring (cut this from a piece of rubber tubing). To measure the volume which the air occupied, proceed as follows: Secure a burette, fill it with water to the zero mark (also fill the effluent tube to the tip). Then draw enough water from the burette to fill the test-tube up to the rubber ring, and read the amount drawn from the burette. Calculate the volume of air dissolved by 100 c.c. of water at the observed temperature and pressure (?)

### 10. The Evolution or Absorption of Heat by Substances While Undergoing Chemical Changes.

Just as in well-known physical changes some substances evolve heat—e. g., ice in freezing—and others absorb heat—e. g., liquids in evaporating—so in chemical changes some substances *give up* heat and others *absorb* heat. The evolution of heat during the combustion of sulphur, carbon, etc., in oxygen is plainly notice-

able, but in many other instances one cannot become aware by any direct means that heat is absorbed or evolved. Thus when potassium chlorate gives up oxygen, heat is given out just as in the combustion of sulphur in oxygen, but the amount of heat produced is not very large and hence it is not noticed beside the heat furnished by the burner. When potassium nitrate gives up oxygen, heat is actually lost, so that the burner flame must not only furnish heat to maintain the material at the high temperature, but it must also supply the heat which disappears.

The general observation to be drawn from these examples is that there is no general rule concerning the evolution or absorption of heat during chemical changes: some substances in changing chemically absorb heat while others evolve heat. The fact that some substances have to be heated while they react is no indication that they *use up* heat in changing: the heating may be necessary merely to produce and maintain the temperature necessary for the rapid reacting of the substance. That is the case with potassium chlorate, which does not use up heat while it liberates oxygen, but actually *gives up* heat, though not enough to keep itself hot enough to continue to react. With combustible substances, the heat given up is more than enough to keep them at the temperature at which they react, and hence they continue to react (burn) without the aid of heat from another source.

To express the quantity of heat resulting from a chemical change, we add to the chemical equation the amount of heat resulting from the reaction when as many grams of the substance are consumed as the numbers expressed by their symbols. Thus the equation—

$$C + O_2 = CO_2 + 96000 \text{ cal.}$$

is intended to express that when as many grams of carbon as C stands for (that is, twelve) combine with as much oxygen gas as combines with this quantity of carbon (which is 32 grams of oxygen), then 96000 calories of heat are evolved or obtained. Similarly, when we write—

$$2HgO = 2Hg + O_2 - 43000 \text{ cal.}$$

we mean that in the decomposition of as many grams as 2HgO denotes in number (that is, 432) the amount of heat, 43000 calories, disappears—is rendered *latent* within the resulting substances. A *calorie* is the quantity of heat required by 1 gram of water to have its temperature raised 1° C.

It should be noted that these examples of thermochemical equations show that, as the result of chemical changes, heat may either *appear or disappear*. It should be added that the amounts of heat which appear or disappear are very small in some instances.

The thermochemical data for the other reactions mentioned in this lesson are here given merely for further illustration.

1. $2KClO_3 = 2KCl + 3O_2 + 19500$ cal.
2. $2PbO_2 = 2PbO + O_2 + 75400$ cal.
3. $2KNO_3 = 2KNO_2 + O_2 - 61120$ cal.
4. $2H_2 + O_2 = 2H_2O$ (at 18° C.) $+ 136720$ cal.
5. $S + O_2 = SO_2 + 71080$ cal.
6. $4P + 5O_2 = 2P_2O_5 + 739800$ cal.
7. $7Na + O_2 = 2Na_2O + 200520$ cal.

### 11. The Dependence of Chemical Changes Upon Surrounding Conditions.

By this time the student is probably asking the question: what part does the heat play in these chemical changes? Is it to be looked upon as a force that impels the reaction? Since there are so many misconceptions possible concerning the influence of heat on chemical changes, an attempt will be made here to present the fundamental facts to the student before he acquires false ideas.

Substances which react chemically are not made to react by forces acting upon them from without. They react on account of the existence of a natural tendency within them to react. This tendency may be increased or decreased by some condition controlled by the experimenter, but these conditions do not *force* the change to take place; they merely increase or decrease the natural tendency to reaction which resides in the substances.

The tendencies with which chemically reacting substances are impelled to change can be increased or decreased experimentally by only *two* different means: by changing the temperature, or by changing the *concentration* of one of the substances concerned in the change. The "concentration influence" will be discussed in later chapters, but the temperature influence will be considered right here.

### 12. The Distinction Between Heat and Temperature.

*Heat* and *temperature* must be carefully distinguished from each other:—they are not *synonymous* terms for one and the same thing, and, in general, their quantities are *not* proportional to each other.

*Temperature* may be said to be the *pressure* or *tendency* with which the heat in a body tends to leave it,—just as the pressure in an automobile tire is the tendency with which the air compressed in it tends to escape. We may follow this comparison further to advantage: As more air is pumped into a tire, its pressure increases: just so the addition of heat to a substance from which it cannot escape increases the temperature of this space. In other words, the temperature rises as heat accumulates in a given substance. Thus, when an incandescent electric light bulb is wrapped up in paper, clothing, or anything which prevents

the radiation of the heat produced from the electric energy in the bulb, then the temperature of the bulb will rise steadily until some of the material is set on fire and it is destroyed.

### 13. The Influence of Temperature Upon Chemical Changes.

When a substance or a mixture of substances is not changing chemically the forces between the atoms and molecules in it are either prevented from acting by something akin to friction or to an obstruction, or they are perfectly balanced so that there is no excess of force tending to produce a change.

In the first case, raising the temperature frequently lessens or removes the friction or obstruction; hence raising the temperature is the most general means employed for removing such resistances and "facilitating" chemical changes. In many cases, the resistance at ordinary temperatures is so great that the substances do not react at all, while at higher temperatures the resistance disappears and the chemical forces in the substances are then able to propel the change more or less rapidly. The removal of resistance by a rise in temperature is quite regular:—the amount of substances changed is approximately doubled by every rise of 10° C. It is on this account that substances undergoing chemical changes are usually heated. Note the application of this in the experiments already performed.

In the second case mentioned above, a chemical change will take place only when the conditions of equilibrium are changed. This also can be done through a change of temperature. However, a temperature change may displace an equilibrium "toward either side," which means that a change in temperature may increase the reacting tendency of the original substances *more or less than* that of the resulting substances. The latter tend to change in the opposite sense from the original substances, or so as to produce the original substances again—they oppose the reaction of the original substances. Hence, as long as the two opposing tendencies are equal, no change can take place; but if through a change of temperature they become unequal, a change will ensue in accordance with the relation of the two opposed reaction tendencies. This matter will be considered further in connection with the study of special examples of equilibrium presented later on.

### 14. Connection Between an Evolution of Heat from a Reacting Mass and the Strength of the Reacting Forces.

The general result concerning the heat effect accompanying a reaction was stated above in Article 10: the heat effect may be either "negative" or "positive." Hence, in general, there is no direct relation between the heat effect and the forces producing

chemical changes. But when the amount of heat evolved is very large, then there is a rough connection between the heat effect and the forces producing such a change. This is due to the fact that negative heat effects and the forces which produce them are always relatively small; hence, a reacting substance or mixture which evolves a *great* quantity of heat must have most of its forces acting so as to produce this heat—even if some of its forces would produce a (small) negative heat effect—and hence the total acting force and the quantity of heat are roughly proportional to each other (Thomsons Rule). This is illustrated in the reaction of oxygen with sulphur, phosphorus, carbon, and sodium, respectively, in all of which the vigor of the actions indicates that the reacting tendencies are great, and we note the amounts of heat evolved also are great; in other words, they are *roughly* proportional to each other.

The production of great quantities of heat by some chemically reacting substances is due to conditions similar to those which result in the production of heat when a heavy body strikes the ground after falling through the air from a great height. If the body had been attached to a rope, the latter passed over a pulley, and a counterpoise attached on the other end of the rope, then the body would have raised the counterpoise while descending, and thus it would have spent its "energy of position" by performing the work of lifting the counterpoise. It also would have approached the bottom *slowly,* and hence not produced any heat on striking the ground. The energy thus spent in raising the counterpoise is the energy which appears as heat when the body falls freely to the ground.

Substances or mixtures of substances which are capable of reacting with the evolution of much heat possess *potential* energy just as the above body possesses potential energy before its fall. Whenever such substances undergo reaction with the production of heat, they lose this potential energy, and in its place we obtain the heat evolved. But when they are "hitched" up by a suitable chemical mechanism so that they will do work, then none, or very little, heat will appear—just as is the case when the descending stone raises a weight. The galvanic battery is a good illustration of a "hitched up" chemical change: the reaction in the cell can take place only when an electric current is drawn from it, and through this current the reaction is doing work,—e. g., turning a motor, etc.

We note that only a very small amount of heat is evolved in a battery cell when in action, but if the materials of the separate poles in a battery cell are brought into direct contact, then they will react without producing an electric current, or doing work, and in this case their reaction will be marked by the evolution of a large quantity of heat.

**15. Chemical Equilibrium and Its Significance.**

In Article 11 of this chapter it is mentioned that when substances react chemically they are impelled by *internal* forces and not by external forces; and in Article 13 it is stated that a substance or a mixture of substances which is not undergoing a change either has its internal forces balanced, or hindered from action by something akin to friction or to an obstruction. Since resistance or friction can be overcome by suitable means, it follows that every substance or mixture of substances with unbalanced internal forces will react until there is no remaining tendency for reaction. However, when the condition of rest has been attained, internal acting forces are not absent: they are merely balanced: or, in other words, only those substances or mixture of substances need be considered as non-reactive which have their internal forces in equilibrium.

At present we do not know enough about the forces in matter to be able to forecast whether or not a certain substance or mixture of substances will react. Hence, in the effort to learn to forecast whether or not a substance or a mixture of substances will react, chemists content themselves at present with learning, by trial, the conditions under which they are in equilibrium: it follows that, under all other conditions, the substances are not in equilibrium, and hence will react so as to attain equilibrium conditions. Thus, it is seen that the ascertaining of equilibrium conditions is of prime importance in modern chemistry.

This matter of determining equilibrium conditions is simplified immensely by our knowledge that there are only a few factors which affect or determine equilibrium. These factors are:—

(a) The concentration of each substance.
(b) The temperature of the mixture.
(c) The pressure upon the substance.

Furthermore, the concentrations of the substances at equilibrium are limited in their conjoint variation by the "Law of Mass Action," and also the number of physical forms of each substance which may be present at equilibrium is limited by the "Phase Law."

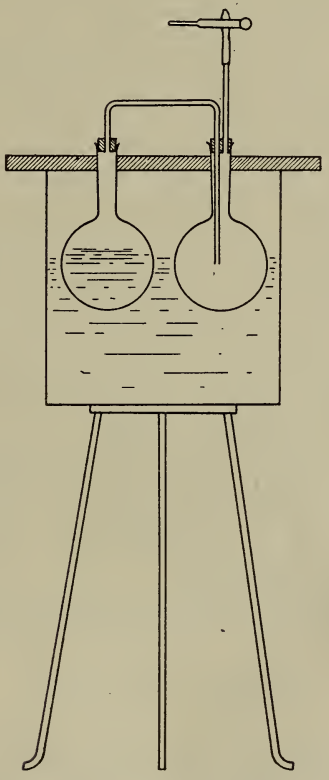
On account of these fundamental facts known concerning the relations of substances at equilibrium, and the further fact that substances when *out of equilibrium* react so as to attain equilibrium, it is evident that equilibrium conditions are the means for deciding whether or not substances or a mixture of substances will react.

The chief characteristic of a substance or mixture of substances under equilibrium conditions is the fact that the substance or mixture can undergo two exactly opposite changes; and that the opposing tendencies are equal. In order to acquaint the student with this, we shall present several examples beginning with a sim-

ple self-evident case, and follow it with gradually more complex cases.

**16. First Illustration of Equilibrium:—The Relation Between the Tendency of a Substance to Change to Vapor and the Reverse Tendency to Condense—Illustrated with Water and Steam.**

**Experiment.**—Secure a water bath or similar vessels of about 2 liters (2 quarts) capacity, and two round-bottom flasks of about 150 to 200 c.c. capacity—which will fit side by side into the water bath. Place a 1″x3″ strip of wood across the water bath and bore two holes in it large enough to fit the necks of the flasks, rip the plank along the line of centers of the holes, insert the necks of both flasks from the same side, and clamp or fasten the two halves of the plank by means of a piece of twine or wire, or by means of two screws driven into the one-inch edge.



Put a one-hole rubber stopper into one flask, and a two-hole rubber stopper into the other. Bend a piece of 7 mm. bore glass tubing so as to fit with one end into the one-hole stopper in one flask, and with the other into one hole of the stopper in the other flask:—this tube should terminate at the "inside" end of the one-hole stopper, while extending nearly to the bottom of the other flask. Put a straight piece of glass

tubing, about four inches long, with one end through the second hole of the two-hole stopper, slip a 2-inch piece of small rubber tubing over the outer end of this straight glass tube, and clamp this with a screw clamp. Fill the flask on the left side of the diagram half full of distilled water. Fill the bath about one-third full of tap water and add enough common salt to saturate it. Put the flasks into the bath, and the latter on a tripod, and heat it to boiling. Keep the pinch clamp off the rubber tubing until a *vigorous* jet of steam issues from the open end of the rubber tube:—then close this with a screw clamp. What becomes of the steam now? Is there none formed now—that is, is the water in the flask boiling? Why not? At most, it will form steam bubbles slowly. Take the flasks out and pour a little cold water over the outside flask:—note whether or not the water is now boiling in the flask. Why?

To describe this fact in technical terms, we say that we are confronted here with opposing tendencies—that of the liquid tending to change the vapor, and that of the vapor tending to change to the liquid form. Concerning these tendencies, we know that at any *fixed* temperature—100° C. in this case—the tendency of a liquid to vaporize is constant, but the tendency of its vapor to condense varies with its own concentration—or pressure: at 100° C., a concentration which gives an aqueous vapor pressure of 1 atmosphere (or enough to support a column of mercury 760 mm. in length at 0° C.) has a condensing tendency just equal to the vaporizing tendency of water at the same temperature, and hence these two forces are in equilibrium. If the concentration of the aqueous vapor is less than that corresponding to a pressure of 1 atmosphere, the tendency for the water to vaporize will be greater than the opposing tendency of the vapor, and the water will change to vapor: vice versa, if the concentration of the vapor is greater, vapor will condense to liquid.

It is seen from the foregoing that the conditions of equilibrium between water and aqueous vapor at any one temperature are completely expressed by stating the pressure of the aqueous vapor formed from water at each temperature. A complete table of these equilibrium conditions is given in the Appendix (see Table of "Vapor Pressure of Water").

The general relations here shown with water exist with every liquid (and even solid) that "vaporizes" appreciably.

### Questions on Chapter II.

1. With what elements does oxygen combine? Is heat given out in all these reactions? Do all compounds of oxygen liberate oxygen appreciably at sufficiently high temperatures?
2. Mention five substances that give up oxygen. Calculate the per cents of their weights obtainable as oxygen gas at sufficiently high temperatures.
3. What is the weight of the resulting oxide produced by

burning 5 grams of sodium? of sulphur? of carbon? of phosphorus? What is hydration? How much water is required to hydrate 5 grams of sodium oxide? of carbon dioxide? of sulphur dioxide? of phosphorus pentoxide?

4. By what means—in general—may the velocities of chemical changes be increased? Where do the forces reside that cause chemical changes?

## CHAPTER III.

## SIMPLE REACTIONS BETWEEN METALS AND ACIDS AND THE PREPARATION AND PROPERTIES OF HYDROGEN.

### 1. The Reactivity of Different Metals.

The first kind of a chemical reaction brought before the student consisted of the decomposition of a single substance, or the combination of two substances into a single substance,—which is the simplest sort of a change that can be found. The second kind of a chemical change to be brought before the student presents the interaction of two substances which result in *two* other substances. For illustration, we have chosen the interaction of some metals with some acids, which results in the liberation of hydrogen from the acid, and in the *formation* of a compound of the metal together with the other components of the acid (i. e., other than the liberated hydrogen). In general the equations for these changes have the form:

$$M + HA = MA + H$$

Here M stands for any of the metals which react thus. HA is used to denote the acid, because in this connection acids may be considered to be made up of only two different components,—hydrogen—H—being one of them, and all the remainder—A—being the other. The latter is frequently called the acid radicle.

**Experiment.**—Put some copper filings into a test-tube and cover them with dilute hydrochloric acid; do the same with cadmium, zinc, tin or lead, and magnesium. Compare the rates of formation of the gas (hydrogen) in these mixtures. Try the accelerating effect of a *rise in temperature* upon those mixtures which otherwise react slowly. Arrange the metals in the order of their reactivity with this acid.

In the same way try the same metals with dilute acetic acid, and again with dilute sulphuric acid. Does the order of the reactivity of these metals remain the same with each of these acids?

When all the common metals are arranged in the order of their tendencies to react with the same substances—to form the common compounds such as oxides, chlorides, sulphates, nitrates, etc.—the following list is obtained:

potassium
sodium
calcium
magnesium
aluminium
zinc
iron

cadmium
tin
nickel
lead
hydrogen
copper
silver
mercury
gold
platinum

The marked differences in the tendencies to reaction exhibited by these metals illustrates strikingly the fundamental fact that substances are impelled to reaction by tendencies inherent within them.

The quantitative relations in the above reactions are expressed as follows:*

| | | | | | | |
|---|---|---|---|---|---|---|
| Cd | + | 2HCl | = | $CdCl_2$ | + | $H_2$ |
| cadmium | | hydrochloric acid | | cadmium chloride | | hydrogen |
| Zn | + | 2HCl | = | $ZnCl_2$ | + | $H_2$ |
| zinc | | | | zinc chloride | | |
| Mg | + | 2HCl | = | $MgCl_2$ | + | $H_2$ |
| magnesium | | | | magnesium chloride | | |
| Cd | + | $2H(C_2H_3O_2)$ | = | $Cd(C_2H_3O_2)_2$ | + | $H_2$ |
| | | acetic acid | | cadmium acetate | | |
| Zn | + | $2H(C_2H_3O_2)$ | = | $Zn(C_2H_3O_2)_2$ | + | $H_2$ |
| | | | | name? | | |
| Mg | + | $2H(C_2H_3O_2)$ | = | $Mg(C_2H_3O_2)_2$ | + | $H_2$ |
| | | | | name? | | |
| Cd | + | $H_2SO_4$ | = | $CdSO_4$ | + | $H_2$ |
| | | sulphuric acid | | cadmium sulphate | | |
| Zn | + | $H_2SO_4$ | = | $ZnSO_4$ | + | $H_2$ |
| Mg | + | $H_2SO_4$ | = | $MgSO_4$ | + | $H_2$ |
| 2Al | + | 6HCl | = | $2AlCl_3$ | + | $3H_2$ |
| 2Al | + | $6H(C_2H_3O_2)$ | = | $2Al(C_2H_3O_2)_3$ | + | $3H_2$ |
| 2Al | + | $3H_2SO_4$ | = | $Al_2(SO_4)_3$ | + | $3H_2$ |

The number of hydrogen atoms that an atom of metal "displaces" is a measure of its combining power and is known as its *valence*. It is a definite number for each particular kind of metal. The equations above show that the valence of cadmium is 2; so is that of zinc and of magnesium; but the valence of aluminium is 3. A more extensive consideration of valence is given in Chapter VI.

*The molecule of hydrogen, just like that of oxygen and of *most* elementary gases, has two atoms in each molecule.

### 2. The General Facts Concerning the Interactions of all Metals with all Acids.

When the reaction is of the simplest sort—as with the acids used above—then only the metals above copper in the list above undergo reaction, while copper and the metals below it in the list have too small a tendency to effect a reaction. But with nitric acid and with concentrated sulphuric acid (in general, with acids capable of oxidizing action), *all metals react except* the lowest in the list—gold and platinum. However, with the latter acids the reactions are more complex than with the acids used above: hydrogen is not liberated, and instead other products are formed. Reactions with these acids will be studied specially later on under the heading of "oxidation and reduction reactions."

**Experiment.**—For the purpose of showing merely that nitric acid and concentrated sulphuric acid react and give products other than hydrogen, treat in different test-tubes a small piece of copper with nitric acid and a small piece of zinc with concentrated sulphuric acid.

The foregoing facts, formulæ, and equations should be committed accurately to memory. The student should also drill himself in working numerical problems similar to the following: How many grams of zinc are required to produce 3 grams of hydrogen gas? How many grams of pure sulphuric acid are required to react with 5 grams of aluminium? How many grams of magnesium chloride can be obtained with 10 grams of magnesium?

### 3. The Preparation and Collection of Hydrogen and a Demonstration of Some of Its Properties: a Practical Application of the Reactions Between Metals and Acids.

**Experiment.**—Two students may work together on this experiment. Fit a 400-600 c.c. flask with a two-hole stopper (rubber), a long-stem funnel, and a delivery tube as in Fig. A. Put a handful of granulated zinc into the flask, cover this with water and connect up the apparatus. Secure a water basin, three wide-mouth bottles and glass covers. Add small portions of concentrated hydrochloric acid to the flask through the long-stem funnel until a brisk formation of hydrogen occurs. Allow the gas to escape until the air has probably been swept out of the flask, then fill the three bottles with the gas, and place them mouth downward on the glass slides.

After filling these three bottles, attach a glass "nozzle" to the delivery tube, light the issuing gas jet, and let the flame burn below a large beaker or flask filled with cold water: the condensed water is due to the reaction—

$$2H_2+O_2=2H_2O$$

Reduce the size of the flame of one of the gas burners, and then lower one of the bottles of hydrogen down over the flame—to ascertain if the gas flame continues to burn in the hydrogen.

Pour hydrogen from a bottle upward into another bottle filled with air and held mouth downward to catch the hydrogen (see Fig. B). Test

with a flame to ascertain if the gas has passed from the lower to the upper bottle.

The hydrogen in the third bottle is to be mixed with approximately

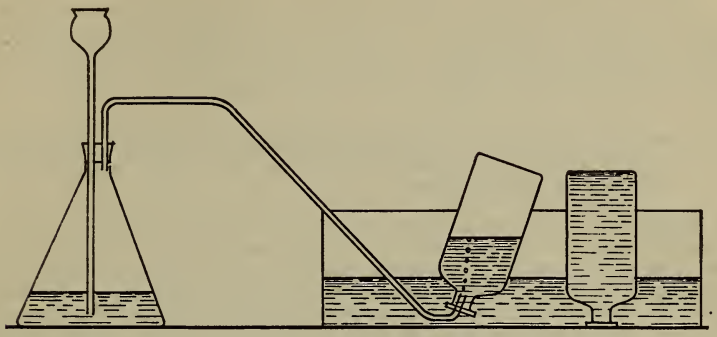


Fig. A.

one-half its volume of oxygen, and the mixture to be exploded—for this purpose secure a suitable bottle full of oxygen, place the hydrogen bottle

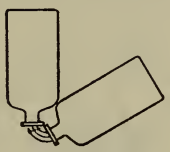
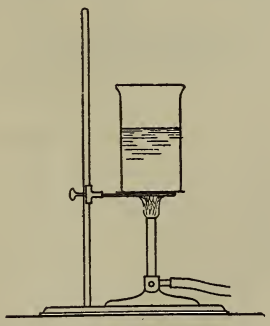


Fig. B.

mouth downward over the oxygen bottle, remove the glass covers, invert the bottles together to hasten the mixing of the gases and then ignite the mixture.



Correct heating.

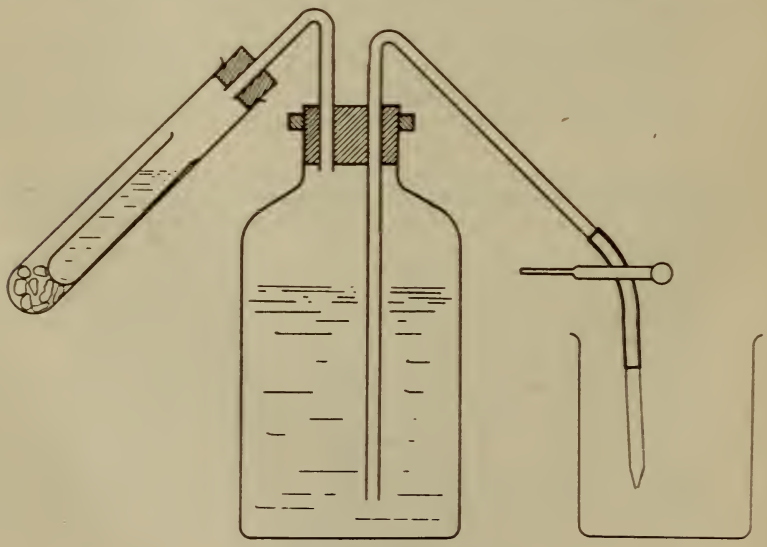
Decant a small portion of the spent liquor from the generating flask into a small evaporating dish, put this dish on an iron ring-stand with a piece of asbestos board under it, and evaporate the liquid by heating it moderately with a Bunsen burner.

Do the same with 1 c.c. of dilute hydrochloric acid. Note that the latter leaves no solid residue, while the former leaves a residue. Infer what the residue is.

In your note book make suitable entries of the observation made in this experiment. Note that incidentally the experiments have indicated something concerning the solubility of the gas in water,—its specific gravity,—color, and odor.

**4. Determination of the Relative Amount of Hydrogen Formed by the Simple Interaction Between an Acid and a Metal (Zinc and Hydrochloric Acid).**

**Experiment.**—Secure a bottle of one to two liters capacity, "narrow mouth"; e. g., a bottle in which acids and ammonia are ordinarily supplied in commerce. Fit it with a two-hole rubber stopper. Secure a 7 mm. bore glass tube of such length that it may extend to the bottom of this bottle, and about 6 inches outside: bend the tube so that the outside end will form an angle of 45° with the other end. Secure another piece of glass tubing, about eight inches in length, bend at the midpoint also to form an angle of 45°, and insert one end into the two-hole stopper so that it will terminate inside of the bottle just below the stopper. To the other end of this shorter tube, fit a one-hole rubber stopper which fits a specially wide test-tube to be secured for this purpose.



The outside end of the other glass tube—that is, the one which extends to the bottom of the bottle—is to be fitted with about ten to twelve inches of small pliable rubber tubing, and the other end of this tubing is to have a small glass nozzle attached to it. A pinch clamp is put on the rubber tube.

Weigh out accurately about 1 gram of *pure* zinc, and place this in the bottom of the large test-tube. Then secure a short, small test-tube, and

put into it about 10 c.c. of concentratel hydrochloric acid plus an equal volume of distilled water. Add one drop of a copper sulphate solution: this is for the purpose of producing a trace of copper metal on the zinc—which will "catalyze" the action between the zinc and the acid.

Lower the small test-tube carefully into the large test-tube (after inserting the zinc in the latter!). Fill the large bottle two-thirds full of tap water, insert *tightly* the stopper with the glass tubes, drain the water through the nozzle until the rubber tube and nozzle are full of water, then close the pinch clamp on the rubber tube. Fit the large test-tube with its contents securely to the one-hole rubber stopper on the connecting glass tube. Secure a large (600 c.c.) beaker, put a small amount of tap water into it. Then put the end of the nozzle under the surface of this water, open the pinch clamp and raise the beaker until the levels of the water in the beaker and in the bottle are at the same height. After holding the beaker there long enough for the pressure of the gas in the bottle to become equal to the atmospheric pressure, close the pinch clamp, pour out all the water in the beaker, put the nozzle again into the beaker, open the pinch clamp and slip it aside so that it will hang on the rubber tubing without clamping the latter.

Next tilt the bottle in order to allow most of the acid to run out into the wide test-tube and hence come in contact with the zinc. Then set it straight up, and allow the action to proceed, being careful to catch all the expelled water in the beaker.

When the zinc has been consumed, raise or lower the beaker to make the pressure inside of the bottle equal to the atmospheric pressure, close the rubber tube with the pinch clamp, and weigh the beaker and water on a coarse or platform balance—to the nearest whole gram. Then pour out the water and weigh the empty beaker.

Ask the instructor to read the barometer. Take the temperature of the water remaining in the large bottle.

*Calculations.*—The net weight in grams of the water is the same as the number of cubic centimeters of hydrogen obtained (fundamental fact of metric system!) The gas was collected over water, at the observed temperature (of the water), and under the observed atmospheric pressure: put your observed results in the note book thus—"— c.c. of hydrogen at —° C. and under — mm. pressure, saturated with moisture." Calculate what volume of hydrogen this would be if dry at 0° C. and under 760 mm. (see Chapter IV, Art. 4). Next calculate how many c.c. of dry hydrogen at 0° C. and 1 atmosphere would have been obtained from one gram—atom of zinc (65.37 grams!).

Next calculate how many grams of hydrogen the latter volume would weigh (see weight of 1 liter below).

### 5. Other Properties of Hydrogen.

When hydrogen and undiluted oxygen are mixed in a suitable burner in the ratio, by volume, of 2:1, a very hot flame is obtained. When mixed and kept at or below room temperature, no perceptible reaction takes place. If the mixture is kept at 300° C. for several days, a very small amount of reaction will take place. At 518° C. several hours are required for complete reaction, but at 700° C., and above, reaction is almost instantaneous. When the mixture is kept at very high temperatures (2000° C. and above) equilibrium is reached while some of the oxygen and hydrogen are still uncombined.

Finely divided platinum, palladium, iron, and iron oxide

"catalyze" the reaction between hydrogen and oxygen—so that the latter will combine *fairly* rapidly even at ordinary temperatures when in contact with one of these "catalyzers."

A liter of hydrogen at 0° C. and 760 mm. weighs only 0.0987 grams. It is the lightest of all known gases. Air is 14.5 times as heavy. Hydrogen has been liquefied (boiling point,—252.5° C.) and solidified (melting point—260° C.). Hydrogen is absorbed by many metals (platinum, palladium, iron, gold) and this action explains the catalytic effect that these metals have upon mixtures of hydrogen and oxygen.

### Questions on Chapter III.

1. Name several metals any one of which when put in contact with any one of several acids—also to be named—react so as to give hydrogen and a compound of the metal with the components of the acid other than the hydrogen. How many grams of each of the metals named are required to produce 5 grams of hydrogen? How many grams of each of the acids are required to produce 5 grams of hydrogen? It is understood that the water with which the acids are mixed (in which they are dissolved) is not to be included in the weights.

2. State the general facts concerning the interaction of *all* metals with *all* acids.

3. State the properties of hydrogen which were demonstrated experimentally before you.

## CHAPTER IV.

## THE MOLECULAR-KINETIC STRUCTURE OF GASES AND OF CONDENSED FORMS (LIQUIDS AND SOLIDS).

### 1. Introduction.

The chemical and physical study of substances in their three different forms have revealed that the gaseous form is not only the simplest in structure and behavior, but that the molecular structure and most properties of all gases are exactly the same. Hence, we shall consider gases first.

### 2. The Structure of Gases.

A gas consists of small particles (molecules) separated by relatively wide, empty spaces. The molecules are constantly moving, rapidly, in straight lines and change direction merely whenever they hit other molecules or some solid or liquid obstruction. This constant motion or flight of gaseous molecules is the cause of the rapid diffusion or spreading of unconfined gases through unoccupied space,—hence, also the cause of their diffusing into other gases (because the greater part of a gas volume is not equipped by molecules).

**Experiment.**—*Demonstration of the Diffusion of Gases.* (To be performed by the instructor.)

We shall employ hydrogen and air to demonstrate the diffusing tendency of gases. Since the mass of the hydrogen molecule ($H_2$) is only 2 atomic weight units, while that of the nitrogen (which is 80 per cent of the air) has a molecular mass of 28, it follows that, at the same temperature, their molecular velocities have the relation (see Article 3a)—

$$\tfrac{1}{2}(2)v^2_{hydr.} = \tfrac{1}{2}(28)u^2_{nitr.} \text{ or}$$

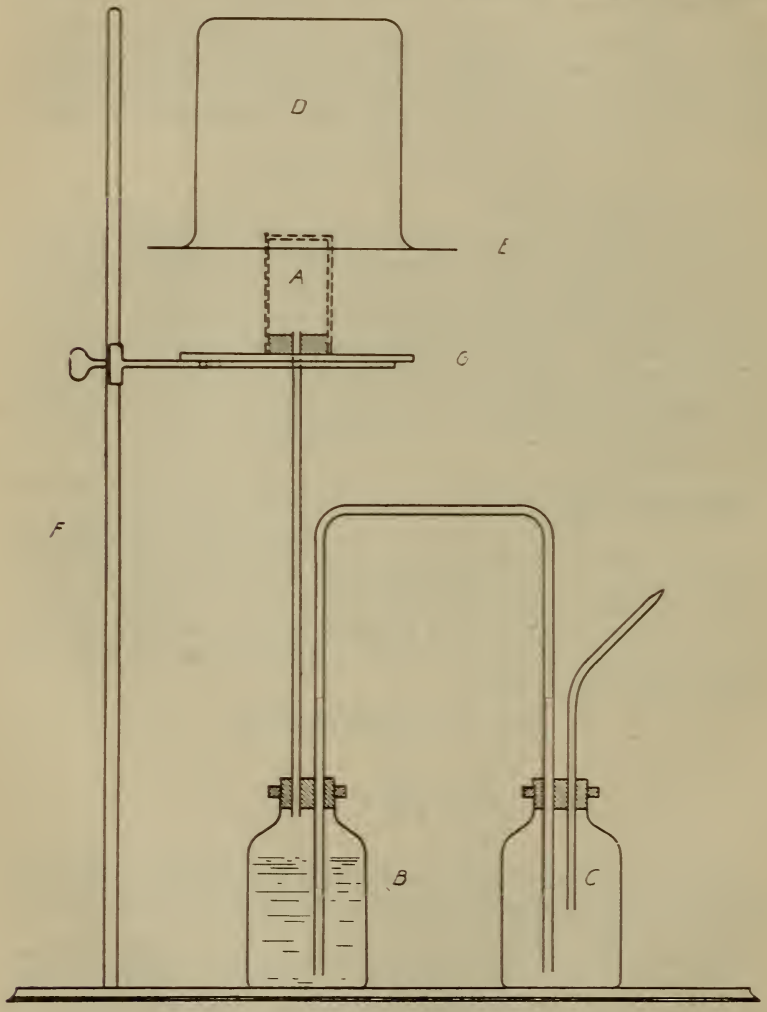
$$\frac{V_{H_2}}{V_{N_2}} = \sqrt{\frac{28}{2}} = 3.7+$$

Hence, if we put hydrogen and nitrogen at opposite ends of a tube, 3.7 times as much hydrogen as nitrogen will pass through during the same time.

For our tubes we shall employ the pores in a 1 quart porous earthenware "battery jar" (see A in accompanying figure). This is closed securely with a rubber stopper, and connected with bottles B and C by means of glass tubes—as shown. B is filled with colored water. F is a large iron ring support, and G is a plank with a small hole drilled in the center. E is a piece of cardboard perforated to fit A. D is a large beaker of a bell jar, which

has been filled with hydrogen over water, and is then transferred (with the aid of pane of glass).

E is pushed down with the bell jar on it. Immediately, the colored liquid in B will be blown over into C, and some of it blown out of C, through the nozzle. When the pressure has spent




itself, the bell jar is removed: the liquid will then be drawn from C back into B.

The cause of the pressure and suction is the difference in the velocities of the molecules of hydrogen and air, respectively. With

this suggestion, the student should be able to explain the actions in the experiment.

### 3. Quantitative Relations in the Behavior of Gases.

(a) At the same temperature, the velocities of zig-zag flight (vibration) of the molecules of different gases are such as to give to the molecule of each gas the same average *kinetic energy* ($\frac{1}{2}$ m $v^2$).

(b) At the same temperature, and under the same pressure, equal volumes of all gases contain the same number of molecules. (Avogadro's Law.) This number is $2705 \times (10)^{16}$ molecules in 1 c.c. at 0° C. and 760 mm. pressure.

(c) If the effluent tube of an automobile air pump is closed, and the piston is forced down half way from the top, then all the molecules which at first occupied the whole pump cylinder will be confined in half the volume:—a little thought will reveal that each molecule now has only half as far to travel to hit the piston head, and hence it will make twice as many hits per second than it did when the piston head was at the top; and the pressure on the piston head is twice as great as it was when the piston head was at the top. This relation between the volume and the pressure of a gas is *perfectly general*, and is expressed thus (at the same temperature) the pressure of a definite amount of gas varies inversely with its volume (or vice versa). This is known as the Law of Boyle.

(d) When a gas has its temperature raised (or lowered), then the velocity of flight of its molecules is increased (or decreased) to exactly such an extent as to change either the volume "v" only —or the pressure "p" only—or their product (pv)—by $\frac{T_2}{T_1}$, where $T_1$ denotes the original temperature (measured on the Absolute Scale) and $T_2$ the final temperature. This is known as the Law of Charles. The Absolute Scale reading is derived from the centigrade scale reading by adding 273.1° to the latter.

### 4. The Reduction of Gas Volumes to Standard Conditions.

The Laws of Boyle and Charles make it possible to find, by calculation, the volume occupied by a gas under any desired condition of temperature and pressure if its volume at one temperature and pressure is known. For example, if we have 50 c.c. of a (dry) gas at 26° C. and 750 mm., and we wish to know what volume this amount of gas will occupy at —10° C. and 710 mm., we proceed as follows: We can calculate the effect of either influence first—let us take the pressure first: The gas changes

from a greater to a lesser pressure—hence it will expand—and we must multiply by an improper fraction formed from the two pressures—that is, by $\frac{750}{710}$, which we indicate by $50\times\frac{750}{710}$

The volume of the gas now is $(50\times\frac{750}{710})$, and the temperature effect on this volume is obtained as follows: The change will cool the gas and *lessen* the volume,—hence we must multiply by a *proper* fraction formed by the two temperatures—that is, by

$$\frac{273+(-10)}{273+26} = \frac{263}{299} \text{ and we obtain } (50\times\frac{750}{710})\times\frac{263}{299}$$

Frequently gases are collected and measured "over water"; that is, saturated with water vapor; and it is desired to know what volume they will occupy *when dry*. To calculate this reduction in volume, we make use of the fact that liquids evaporate into spaces occupied by other vapors or gases as though the gaseous space were a vacuum. Thus, when oxygen, or hydrogen, is collected over water at 26° C., aqueous vapor will be mixed with the oxygen or hydrogen to such an extent that the aqueous vapor alone would produce a pressure of 25 mm. (see Appendix, Table of "Vapor Pressures of Water").

Now, if the aqueous vapor molecules are producing—or supporting—25 mm. pressure, then the oxygen molecules are supporting only the remaining part of the pressure. If the total pressure is 750 mm., then the oxygen is really only under 725 mm. pressure, and hence 725 instead of 750 would be used in making any further calculations as per example above.

*Problem:* Calculate what volume 25 c.c. of air collected over water at 20° C. and 740 mm. would occupy *dry*, at 0°, and 760 mm.

### 5. The Condensation of Gases to Liquids.

Nothing was said in the foregoing about an attracting force acting between the molecules of gases, yet such forces are always present and frequently quite effective. However, they are effective only through very small distances—i. e., the attractive forces between two molecules is appreciable only during the time that they are very close together. With such gases as hydrogen, oxygen, nitrogen, etc., under atmospheric pressure (or less) and at room temperature (or above), the attractive forces between the molecules do not affect the behavior of the gases appreciably.

But if the molecules of these gases are brought closer together, particularly at temperatures far below 0° C., at which the velocities of the molecules are greatly reduced, then the attractive forces affect the behavior of even these gases. With sufficient compression, or lowering of temperature (or both), the attracting forces will become sufficiently extensive to retard the molecules in their flight and to hold them together—then the gases are liquefied.

It must not be thought, however, that the molecules lose all their kinetic energy when a gas is liquefied: they lose a part which appears in the "latent heat" of condensation, but they retain the greater part of their energy of motion and continue to move—though only in close contact with other molecules.

A little reflection will reveal that all the molecules of a substance cannot have exactly the same velocity because collisions change the velocities of the colliding molecules (which is illustrated in the collision of billiard balls), and the velocity we ordinarily speak of is an average velocity possessed very nearly by most molecules. Hence, in the surface of every liquid there will be some molecules which through collisions receive sufficiently great velocities to overcome the attractive forces of the other molecules, and to fly into the gaseous space above. As long as they are there sufficiently far away from other molecules of their kind, these "vaporized" molecules will remain in the gaseous space; but since some of them will collide with some of their own kind, some of the "vapor" will be condensed. The number of molecules thus condensed will become larger as the number of molecules in the vapor becomes larger, until finally the number condensed will be equal to the number vaporized in the same space of time: then we have equilibrium. Thus equilibrium is seen to be the result of two oppositely directed changes taking place at the same rate.

It is seen from the foregoing that molecules of liquids are close together—they practically touch each other; and the molecules hold together by mutual attraction. However, since every molecule is entirely surrounded by molecules of its own kind, it experiences no restraint from this molecular attraction because the attractions on opposite sides balance each other. Since their straight line flight is confined to very short distances, their motion may be properly called "vibration"; yet, through the recoil at different angles—experienced in their "vibrations"—they slowly move through the mass of the liquid in all directions.

### 6. The Vibration of Atoms Within the Molecule.

Although the atoms constituting a molecule are held together securely by their mutual attraction, yet the behavior of substances indicates that the atoms in a molecule are not rigidly *fixed* with

reference to each other, and that they are moving to and fro within a limited space. Just like the "vibratory" motion of molecules, so this vibratory motion of the atoms also is increased by a rise of temperature and hence a gradually increasing number of them will attain such high velocities as to fly beyond the confines of the molecule they are in: this phenomenon, known as dissociation, is quite general, but is observed with only a few substances at ordinary room temperatures, and does not affect many substances appreciably even at high temperatures. Thus steam is dissociated only .02 of one per cent at 1500°C. and only about 1 per cent at 2000°C. Substance with high melting points, e. g., most rocks and minerals, are still less readily dissociated than gases, so that in most cases the dissociation does not become *directly* noticeable: this is because the products formed tend to react in the reverse sense, and mere traces of the products are enough to stop further dissociation, i. e., they produce equilibrium. The part that such slight dissociation plays in chemical reactions is considered and illustrated in the next chapter.

### 7. The Solidification of Liquids: Amorphous and Crystalline Solids.

When liquids have their temperatures reduced, the "vibratory" motion of their molecules gradually becomes less, the attractive forces become more effective, and the mass as a whole becomes more viscous. This is strikingly illustrated in the cooling of molasses, and of pitch: when cold, these materials have the appearance of solids, but, in reality, they are merely extremely viscous liquids. Since they have no particular geometric form, they are called amorphous solids.

Many other liquids behave quite differently on cooling: long before they become appreciably more viscous, they begin to form pieces with specific geometric forms—that is, forms having definite angles between the planes. With pure liquids, this formation of crystals takes place at sharply defined temperatures. Thus, water freezes at 0° C. The change is accompanied with the liberation of heat, which is due to the fact that the crystallized molecules have given up a large part of their molecular velocity and remain almost (not quite) motionless in the place within the crystal which they have taken.

This sudden arresting of molecules takes place only when molecules have had time and opportunity to place themselves in an orderly manner besides others of their own kind, similar to bricks in a wall. Such regular internal "structure" is characteristic of crystals, and differentiates them from amorphous solids. Another characteristic of crystals is the sudden transition from hard crystals to limpid liquid, at a sharply defined temperature,—while

amorphous liquids soften gradually through a long range of temperature.

**8. Dissolved Substances: Solutions.**

Everybody is familiar with the fact that liquids *wet* solids,—which shows that there is a direct attraction between the molecules of the liquid and the solid. In many cases this attractive force succeeds in dislodging single molecules or larger particles from a solid and surrounding them completely with molecules of the liquid: such a resulting aggregate is called a solution. If, in this action, the liquid separates the solid into *single* molecules, then the solution is a *true* solution; but, if the particles are composed of several or many molecules, the solution is known as a colloidal solution,—and the dissolved substance is called a colloid. Ink and liquid glue are familiar examples of colloidal solutions, while sugar-water and salt-water are examples of true solutions.

In ordinary dilute solutions, the particles of dissolved material (called *solute*) are relatively as far apart from each other as the molecules of moderately compressed gases,—hence they do not attract or affect each other to any great extent, and, furthermore, this attraction is balanced on all sides and thus neutralized. The solvent molecules also do not affect them because they surround the solute molecules completely and the molecules on opposite sides neutralize each others' "pull." Hence, *within* the body of the solution, there is nothing that restrains the motion of the solute molecules, and they move freely in accordance with the kinetic or temperature impulse.

Since the free space in liquids is extremely small, the solute molecules are colliding rapidly with other molecules and their main motion is a sort of vibration, yet in addition to this they move slowly through the liquid in all possible directions. The latter slow motion is called *diffusion*.

**9. Boiling Points, Freezing Points, and Osmotic Pressures of Solutions.**

Solutions of solids have boiling points higher than those of their pure solvents: a saturated solution of common salt (sodium chloride) boils at 108.8° C. The rise increases with the relative amount of salt contained in the solution.

Solutions of solids have vapor pressures lower than those of their pure solvents at the same temperature. If a pan of pure water, and a solution of common salt are placed under the same bell jar, the pure water will gradually evaporate and be condensed into the salt solution because the gaseous space will be filled with vapor from the pure water at a pressure greater than that exerted by the salt solution, and hence water will be condensed in the latter until all the pure water has vaporized.

Some substances are so extremely soluble as to form a solution on their surface whenever sufficient aqueous vapor is in the air around them. The action is identical with that in the "bell jar" illustration above. This phenomenon is frequently observed with candy exposed to the air. Substances which have this property are said to be "hygroscopic" or to "deliquesce."

The boiling points of solutions of gases or liquids in (other) liquids may be either higher or lower than those of the pure solvents: they show all possible relations, and each mixture must be studied by itself. The same is true of their vapor pressures when compared at the same temperature.

The freezing points of solutions are lower than those of their pure solvents: a saturated solution of common salt in water freezes at —22° C.

When a solution (e. g., of sugar in water) is put inside of a bag of certain animal or vegetable tissues, such as fish bladders, parchment paper etc., and the whole bag is immersed in the pure solvent (e. g., water), the latter will be drawn into the bag. The material of the bag has no noticeable pores or holes in it: it simply "soaks up" water on one side and gives it up again to the solution on the other side. Looked at from the outside, the phenomenon appears to be actuated by the solute tending to spread into a larger volume of solvent: the force which *appears* to be impelling the solute to attain a large volume is called *osmotic pressure.*

### 10. Compounds of Solvent with Solute.

When "commercial" soda-ash (composition, $Na_2CO_3$) is dissolved in water until a saturated solution is obtained, and the latter is then allowed to evaporate, crystals will be obtained which when heated will give up a great deal of water: their composition is expressed by the formula $Na_2CO_3$, $10H_2O$. The ten molecules of water thus united with every molecule of $Na_2CO_3$ are called *water of crystallization.* The crystals of many salts contain definite numbers of molecules of water, the numbers ranging from one to twelve.

There is evidence which shows that even in solution many solute molecules have "water of crystallization" combined with them, but we do not ordinarily become aware of this combination.

Since crystals containing water of crystallization are definite chemical compounds, they form a vapor with definite equilibrium pressure at each temperature—just as pure water (see Chapter II, Art. 16) or any other single, pure substance does. Although the vapor from these crystals is composed of water only, yet this is sufficient to hold the equilibrium with the crystals as long as some of the *dry,* solid material necessary to complete the composition is present—mixed with the crystals.

If crystals which contain water of crystallization are in contact

with air containing *less* water vapor than that corresponding to the crystals' vapor pressure, the crystals will lose water and break up, forming a fine powder: they are said to "effloresce." This is strikingly illustrated by soda crystals (sal soda or, washing soda, $Na_2CO$, $10H_2O$), which, during dry weather, change to a white powder.

**11. Second Example of Equilibrium: The Dissolution of a Solid in Water Illustrated with a Determination of the Solubility of Potassium Nitrate.**

Secure about 25 grams of potassium nitrate, and crush it as fine as possible in a clean dry mortar. Put the powder into a folded piece of paper and from this pour it into a small flask. Add about 30 c.c. of distilled water, stopper the flask with a clean cork, and shake it fairly vigorously for at least five minutes. A part of the crystalline material should remain in solid form. Secure a thermometer and note the temperature of the solution.

Then secure a clean burette and a clamp to fasten it on the iron ring-stand, pour the solution just prepared into the burette, being careful to fill the nozzle by running some of the solution back into the flask and then pouring this again into the burette, always retaining the undissolved crystals in the flask. For directions concerning the "reading of the burette," see figure, Chapter VI, Art. 2. Then secure a small evaporating dish, clean, dry, and weigh it accurately, and note the weight on a slip of paper. Then pour about 15 c.c. of the solution into the dish, and note the amount taken. Weigh the dish and contents promptly and then place the dish and contents on top of a hot water bath for gentle evaporation.

While the solution is evaporating, proceed with some other experiment. When the content of the dish is dry, wipe the outside of the dish clean, and weigh the dish and contents. Subtract the weight of the empty dish and thus secure the weight of the salt in the amount of solution taken. Calculate the amount of salt in 100 c.c. of solution saturated at the observed temperature. Subtract the weight of the salt from the weight of the solution, thus finding the weight of water which dissolved the weight of salt obtained at the observed temperature.

Calculate the amount of salt dissolved by 100 c.c. of pure water. Also calculate the weight of 1 c.c. of solution:—this is the specific gravity of the solution at the temperature at which it was measured. Put all of the numerical results and calculations into your note book.

Compare your numerical results with those obtained by other members of the class.

Put the remainder of the solution back into the flask with the remaining crystals, place the flask on a wire gauze on the ring-stand, heat it and shake it at intervals. Note that this salt is much more soluble in hot water than in cold water. Set the flask and contents aside to cool—or, if necessary, hasten the cooling by allowing cold tap-water to run over the outside of the flask; some of the salt will crystallize out as the solution cools, and when the solution has cooled to the former temperature, it will contain only as much of the salt as it held before it was warmed. To avoid wasting this "fairly expensive" salt, return the crystals and remaining solution to the instructor.

We may consider that this experiment reveals the action of two

oppositely directed tendencies:—one is the dissolving tendency of the crystals; the other is the tendency of the dissolved salt to *separate* from the solution. Except for the presence of solvent here, this phenomenon resembles that shown in our first example of equilibrium,—the crystals here taking the place of the water in the first example, and the *dissolved* material taking the place of the steam.

Before discussing this phenomenon any further, we must introduce here a fundamental fact concerning the change of activity of a substance:—*at constant temperature, the activity of any substance depends on its concentration, and in most cases varies directly with its concentration.*

The concentration of a substance is the weight of a given amount divided by the volume it *occupies* "uniformly." If the substance is in the gaseous or in the dissolved form, its volume is that of the whole gas space, or solution space, because it extends uniformly into all these parts. If it is a solid (or a liquid), we must subtract the volume of any unfilled "recesses."

Gases and dissolved substances can have their concentrations varied very extensively,—accordingly the activity of a gas or of a *dissolved* substance may have greatly different values.

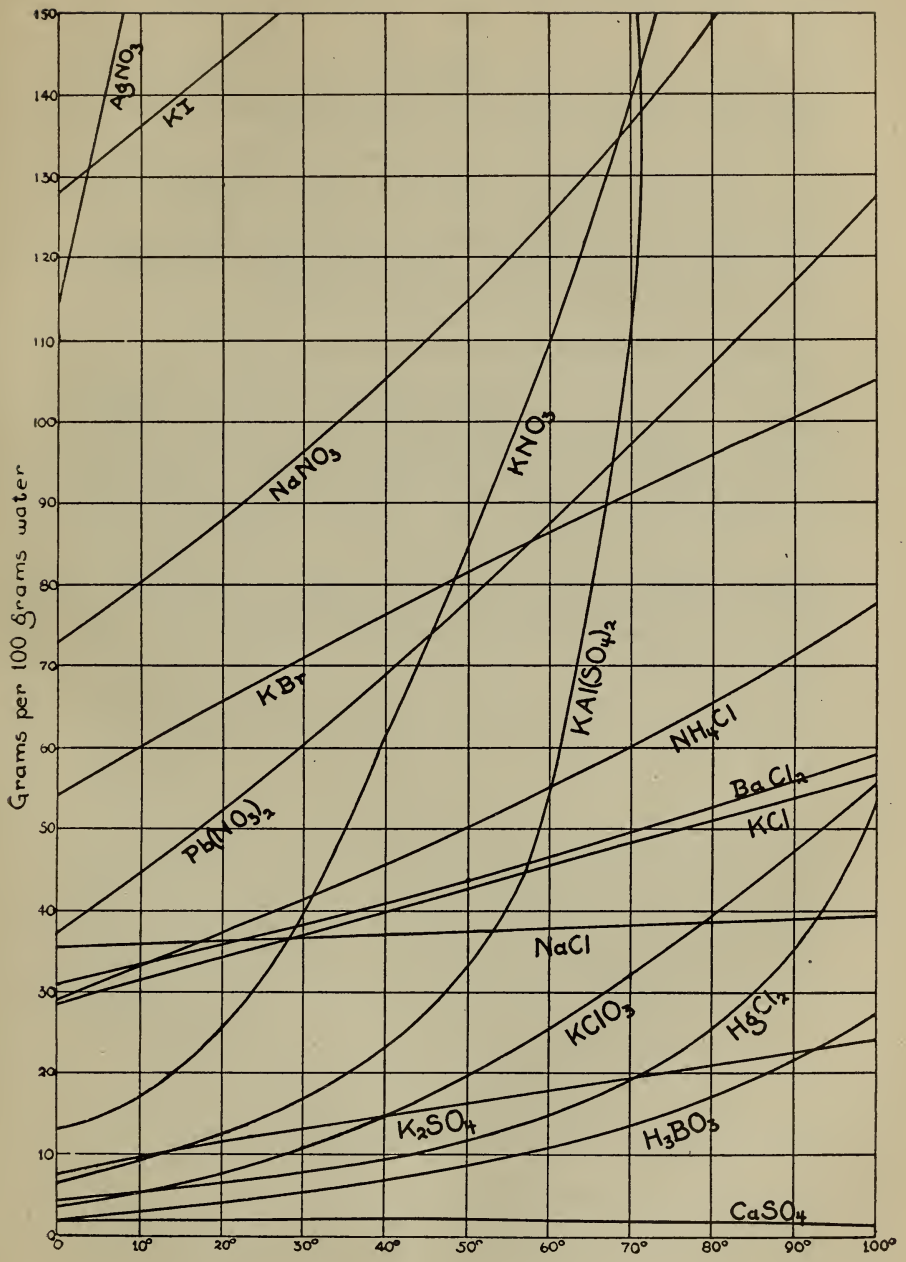
Solids and *liquids* (not the *dissolved* substances) have practically always the same concentrations at any particular temperature,—hence at any one fixed temperature, their activities are practically always the same.

With this information, we may now resume the discussion. Evidently, the crystals have a fixed activity or dissolving tendency at the temperature at which the solution was first prepared; but the tendency of the dissolved portion to "form crystals" increases with its concentration until the two are equal: then we have equilibrium. Crystals are then neither dissolved nor formed (or looked at in another way, just as much of the crystals is dissolved per second as is separated from the solution in the same time).

The experiment also shows the effect of temperature upon this equilibrium:—it shows that, at higher temperatures, equilibrium requires more of the potassium nitrate to be present in the solution. We say, technically:—the equilibrium has been shifted toward the "solution" side, meaning thereby that relatively less of the potassium nitrate will remain as crystals. This *shift* is identical *in* sense with the temperature shift of the first example of equilibrium. Why?

### 12. Relation Between Solubility and Temperature.

The foregoing experiment showed an example in which the solubility of the solid increases with temperatures. From our general experience in this world, we are likely to jump at the conclusion


Grams per 100 grams water
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
AgNO3
KI
NaNO3
KNO3
KBr
KAl(SO4)2
NH4Cl
BaCl2
KCl
Pb(NO3)2
NaCl
KClO3
H3Cl2
K2SO4
H3BO3
CaSO4

that a rise of temperature always increases the solubility of a solid:—while this is true in most cases, yet it is far from being true in all. One of the most common substances—common salt, sodium chloride—has so slight an increase in solubility with temperature that the increase is frequently neglected. Gypsum and lime are less soluble in hot water than in cold.

The curves on the opposite page show the number of grams of each of several salts required to saturate 100 c.c. of water throughout the range of temperature from 0° to 100° C.

The effect of temperature changes upon the solubilities of gases or liquids in (other) liquids is still less regular than that of solids, and each case must be considered specially.

### 13. Recrystallization as a Means of Purifying a Solid.

When crystals are formed from liquids, each kind of material forms its own crystals: no other molecules seem "to fit" into the structure. Furthermore, if we start with a solid mixture of two or more different substances, and dissolve it in hot water until one of the substances saturates the solution, then, on cooling it, we will obtain pure crystals of the *saturating substance only*; provided, that none of the other substances are present in sufficient amounts to saturate the solution with respect to themselves. It should be observed that, as a rule, each substance dissolves and saturates the solutions without being greatly affected by the presence of the others.

## CHAPTER V.

## A REVERSIBLE CHEMICAL REACTION—THIRD ILLUSTRATION OF EQUILIBRIUM.

### 1. Introduction.

For the first two illustrations of equilibrium, we presented changes which are as simple as any that could be secured—the vaporization of a liquid, and the dissolution of a solid. These changes are usually spoken of as *physical changes;* but since the forces of nature are not limited, in their application, by the boundaries set by man between the domains of physics and chemistry, these illustrations show the same relations and forces that are shown by strictly chemical changes.

However, for the next, more complicated example, we shall present a purely chemical phenomenon. But before the equilibrium conditions can be considered, some of the experimental data must be presented separately. These data also are important on their own account.

### 2. The Action of Metals on Water (Steam)—A Further Illustration of the Different Reactivities of Metals, and of the Influence of Temperature Upon Reaction Tendencies.

The very reactive metals in the upper part of the list of metals in Chapter III are so reactive that they displace hydrogen from water. Those highest in the list (potassium, sodium, calcium) are so reactive that their rate of reaction with *cold* water even is quite rapid.

**Experiment.**—(a) To demonstrate the foregoing remark, fuse up one end of a short piece of glass tubing, "pack" into the bottom of this tube some "clean" sodium. Then secure a clean porcelain dish, fill it with distilled water, drop into it a piece of red litmus paper, and invert in it a test-tube filled with water. Drop the "sodium" tube into the water, and place the mouth of the inverted test-tube right down upon the open end of the "sodium" tube, and collect the hydrogen. (If the sodium escapes to the top of the water, turn your face away from the dish until the sodium has been consumed.) Test the gas collected to see if it is combustible.

The sodium and the water react according to the equation:

$$2Na+2H_2O=2NaOH+H_2.$$

Note that the litmus paper changes color.

In your note book make suitable entries of all observations made in the experiments in this lesson.

Metals slightly lower in the list than sodium—e. g., aluminium and magnesium—have a lesser reactivity: their rate of reaction with cold water is too small to be appreciable; but at a higher

temperature—with hot water—they react rapidly enough for the change to be noticeable.

**Experiment.**—(b) A 250 c.c. round-bottomed flask is fitted with a one-hole rubber stopper and a conducting tube of such length and bent so that the flask may be placed on a ring-stand to be heated and the gas formed may be collected over water, just as hydrogen and oxygen were collected in previous experiments. Care should be taken not to allow the conducting tube to extend beyond the rubber stopper inside of the flask. Put some finely divided magnesium into the flask and then fill the flask and conducting tube *full of water*. Also fill a test-tube with water and invert it in the collecting trough so as to have it ready for collecting the gas.

Note that as long as the water is cold, no action takes place.

Heat the water gradually until it boils and collect the gas that passes over. Show that it is combustible.

Evidently, the rise of temperature has increased the rate of action so that the reaction takes place appreciably at 100°.

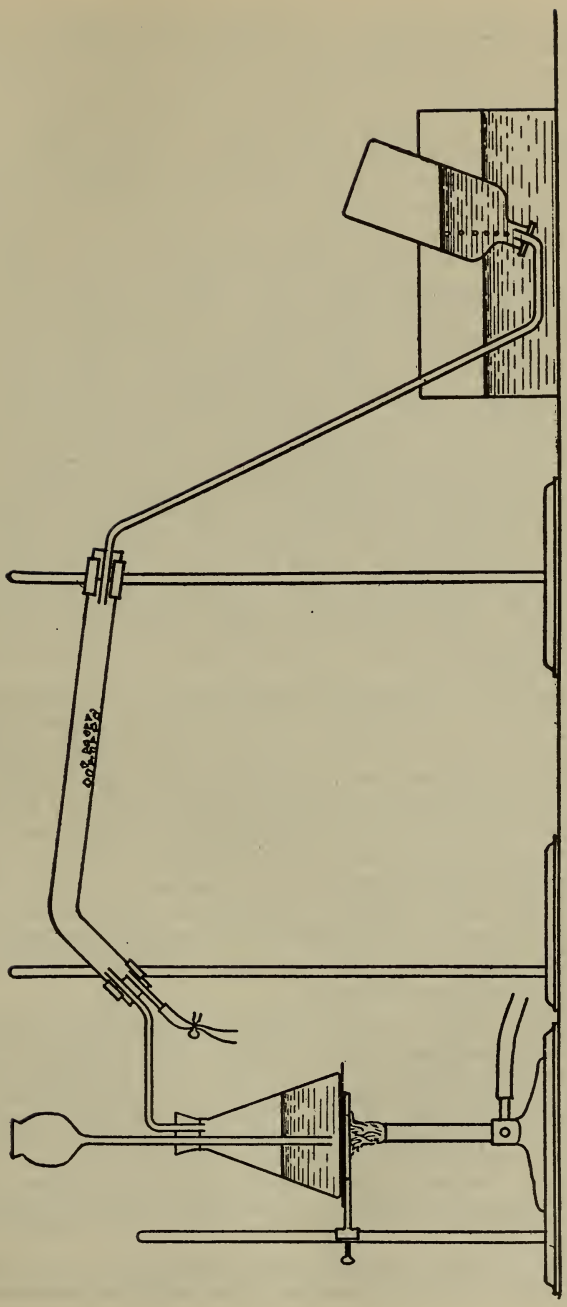
By using water in the form of steam, the reaction may be made to take place at still higher temperatures, and hence a greater velocity will be attained, so that even a metal with a reactivity no greater than that of iron will react rapidly enough for the change to be noticeable.

**Experiment.**—(c) Secure a piece of "combustion tubing" about 50 cm. in length, bend it near the center to an angle of 120 degrees, fit one end with a two-hole rubber stopper and two pieces of very narrow glass tubing, and the other end with a one-hole stopper and an ordinary piece of glass tubing. Secure the flask and fittings used as a hydrogen generator above, but fill it half full with water, and use it to furnish steam. Instead of using—as shown in the figure—a single glass tube connecting the flask to the combustion tube, use *two* short pieces of glass tubing, and connect them with a six-inch piece of rubber tubing. Put some finely divided metal (magnesium ribbon or fine iron filings) into the horizontal part of the tube, and connect up the apparatus as shown in accompanying figure. One of the tubes extending through the two-hole rubber stopper into the combustion tube extends through the stopper at least 8-10 cm., while the other terminates "flush" with the inner end of the stopper; this tube enables the experimenter to remove any water condensed in the cold part of the combustion tube.

Before connecting the boiler to the combustion tube heat the water until a steady stream of steam is obtained. Temporarily discontinue heating the water, but warm up the tube until it is hot enough not to condense steam; then connect the boiler to the tube, and start the steam cautiously through the tube, being careful to keep the tube hot enough not to condense steam, and also being careful to draw off through the extra tubing any water condensed in the lower part of the tube. When everything is in proper working order, heat the tube strongly at the point where the metal has been placed: when the proper temperature is reached the steam and the metal will react rapidly, and the hydrogen formed should be collected in the bottle inverted over the end of the delivery tube. Ascertain if the gas collected is combustible.

### 3. The Reduction of Metallic Oxides:—The Reverse of the Preceding Reaction.

NOTE.—The removal of oxygen from one of its compounds by the action of a third substance—as illustrated in the reaction in this



article—is called *reduction.* The latter term probably originated from the metallurgist's use of the term *reduction* to denote the extraction of metals from their ores: the ores "reduced" in furnaces are generally oxides, and the chemical change consists in the removal of the oxygen by a gas. It is the reverse of oxidation. Besides being used in their primary senses, the terms *oxidation* and *reduction* are also used in more extended senses. The latter will be shown later on.

As might be expected, those metals which have a greater tendency than others to form compounds, exert also a greater resistance to being changed back to the metallic form—they are said to be more difficult of "reduction." The position of the metals in the table given in Chapter III shows their relative ease or difficulty of reduction—the oxides of the metals in the lower part of the list are easily reduced, while the oxides of those in the upper part are hard to reduce. It is on this account that gold and platinum, which are the lowest in the list of metals in Chapter III, are always found in the earth as *free* metals; mercury, silver, and copper are found sometimes as free metals and sometimes as compounds; but the metals farther up in the list are scarcely ever found free in the earth. Again on account of the relative ease or difficulty of reducing their ores (oxides!), the free metals first prepared and used extensively by man were gold and silver, next came copper and tin, then iron and zinc, and only recently aluminum and magnesium.

The molecular dissociation brought about by elevating the temperature, which was discussed in the preceding chapter, is directly responsible for bringing about reaction in the preceding experiment, and hence the latter serves to illustrate this point. When heated, metallic oxides dissociate slightly into free metal and free oxygen. The fraction dissociated is not sufficient to be noticeable because free metal and oxygen gas have a tendency to change backwards, and very small amounts of these two suffice to stop the "forward change." But when hydrogen gas is present, the free oxygen combines with hydrogen and removes the opposing tendency. Then more oxide dissociates; this, in turn, combines with hydrogen, and thus the change continues.

**Experiment.**—Equip a flask for the preparation of hydrogen—as in the preceding experiment. Secure a piece of wide, hard glass tubing—so-called combustion tubing,—30 c.c. in length. Fit cork stoppers into the ends, and perforate the stoppers to suit the connecting tubes shown in the accompanying figure. Secure a "porcelain boat," fill it with copper oxide and insert it into the combustion tube. The copper oxide could be put directly into the combustion tube, but the use of a boat facilitates the operation. Connect the apparatus as shown in the figure, and start the generation of the hydrogen. After the air has been expelled from the apparatus, begin to heat the portion of the tube in which the oxide has been placed.

After the substance has been heated thoroughly in the current of hydrogen, allow the tube to cool, and then empty the substance into a

mortar; note that it has changed color. Try to grind it slightly in the mortar, and note the *metallic streak* obtained.

Repeat this experiment with iron oxide in place of copper oxide. Test the original and the resulting solids with a magnet.

**4. The Determination of the Ratio by Weight in Which Oxygen and Hydrogen Combine to Form Water.**

The reaction which has taken place in this experiment is the following:

$$CuO+H_2=Cu+H_2O.$$

If the boat filled with copper oxide had been weighed before placing it in the tube, and then again after removing it, the difference would have given the weight of the oxygen which has been combined with hydrogen to form water. If, furthermore, the water formed had been collected by passing it through a tube filled with a substance which absorbs *the water only* (e. g., calcined calcium chloride), then the weight of all the water formed with this weight of oxygen would have been obtained by weighing this "absorption tube" before and after the operation. This data would give the ratio by weight in which hydrogen and oxygen combined to form water. By these experimental means all the earliest determinations of this ratio were made—by Berzelius and Dulong in 1820,—by Dumas and Stas in 1843. The following example may serve to illustrate the details of the procedure:

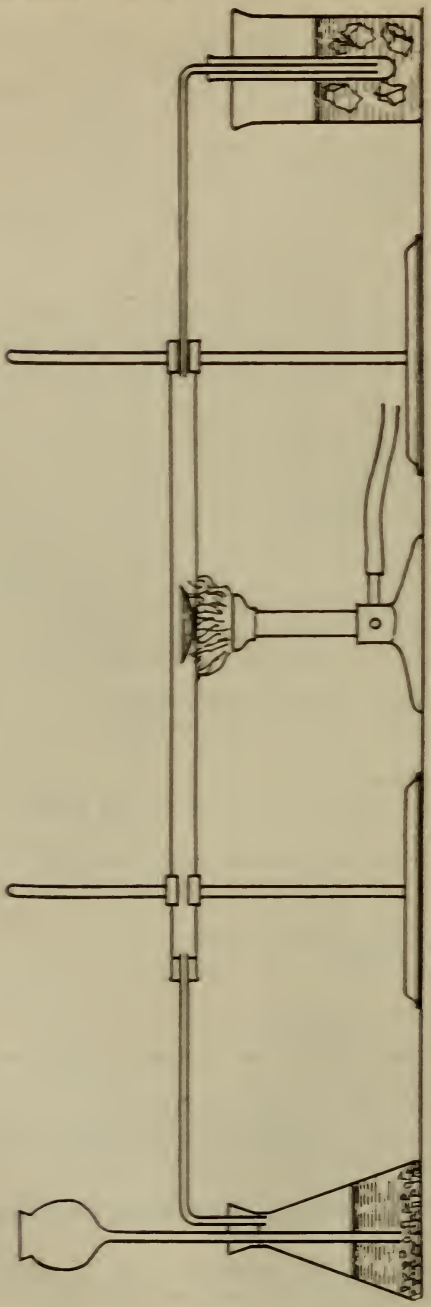
| | |
|---|---|
| Weight of boat and contents before heating | 15.184 grams. |
| Weight of boat and contents after heating | 14.531 grams. |
| Difference, weight of oxygen | 0.653 grams. |
| Weight of calcium chloride tube before the experiment | 36.252 grams. |
| Weight of calcium chloride tube after the experiment | 36.987 grams. |
| Difference, weight of water formed | 0.735 |
| Less weight of oxygen | 0.653 |
| Difference, weight of hydrogen | 0.082 |

Ratio in which hydrogen and oxygen combine to form water: 0.082 : 0.653 :: 1 : 8.

This numerical value is one of the most important ones in chemistry; and the procedure of its determination should be learned accurately by every student in chemistry.

**5. The Equilibrium Between Iron Oxide, Hydrogen, Iron and Steam.**

The main subject of this chapter is now to be considered. It has been shown that hydrogen reduces iron oxide, and that steam



reacts with iron. These two reactions are exactly the reverse of each other because the products formed in either one of these reactions are original materials for the other. Towit:

Iron oxide plus hydrogen form iron plus steam;
Iron plus steam form iron oxide plus hydrogen;

To express this in chemical symbols, we write:

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 3H_2O$$

The upper arrow expresses the first statement, and the lower arrow the second.

If iron oxide and hydrogen are put together into a closed vessel from which the air had been removed, and the vessel and contents are kept at some definite high temperature—say 1000° C.—until all possible changes have run their course,—and hence all parts of the mixture are "in equilibrium" with each other,—then the vessel will contain some of each of the four substances: iron oxide, hydrogen, iron, and steam. If, instead of the substances put in at first, iron and steam are put into the closed vessel, and it is kept at the same temperature until all possible changes again have taken place, then the same four substances will be found within the vessel, and the ratio of the concentration of the steam to that of the hydrogen will be found to be the same as before.

This result comes about as follows: We know from the preceding experiments that both pairs of substances have tendencies to react; hence both pairs of substances put into the vessel at 1000° C. start to react. But, since the newly-formed pairs of substances have tendencies to change in the reverse senses, they oppose the reactions of the original substances in each case. At first, the force with which they oppose the reactions of the original substances is, in each case, not large enough to stop the latter; but as the original reactions proceed, the reacting tendencies of the original substances become less in amount while that of the resulting substances increase in amount, and finally the opposing forces become equal, reaction ceases, and the substances are "in equilibrium" with each other.

The question now arises: what produces the change in the two opposing reaction tendencies on account of which they are unequal at first, and gradually become equal?

### 6. Law of Mass Action Applied to Chemical Equilibrium.

To answer this question satisfactorily, we must present the fundamental *law* connecting changes in chemical activity with changes in concentration while the temperature remains constant. This is called the Law of Mass Action.

In order to calculate changes in activity, the concentrations of

the changing substances must be expressed in *numbers* of molecules per unit volume (1 c.c. or 1 liter). Since the actual number of molecules in any tangible portion of a substance is too large to be used conveniently, we use a larger unit,—the gram-molecule of each substance, which contains $6\times(10)^{23}$ real molecules.

The gram-molecule of any substance is obtained by taking as many grams of it as the number which expresses its molecular weight.

Thus for a gram molecule of hydrogen, we take 2 grams of it; for steam, 18 grams, etc.

*The law of mass action may be stated as follows: the reaction tendency exerted by any single substance or mixture of several co-operating substances changes directly with the molecular concentration of each substance taking part in the change.*

In order to understand this law, let us use a few mathematical symbols merely to express the relations exactly, and apply the law to the first example of equilibrium we have studied,—the vaporization of water.

Let the symbol of each substance placed in square brackets designate the number of gram-molecules of it contained in 1 c.c., thus $[H_2]$ is to designate the number of gram-molecules of hydrogen per 1 c.c. present in a particular case.

Next, let us express by something like a chemical equation, the reaction which takes place in the first example of equilibrium studied (see Chapter 2): $H_2O$ liquid $\rightleftarrows$ $H_2O$ vapor. The arrows are intended to show that the change is reversible.

We will now consider by itself the reacting tendency of the substance on the left of the equation—i. e., of liquid water:—since it cannot vary its concentration (at any definite and constant temperature!), its reacting tendency is constant, and we will express it by $k$.

Next let us consider the reacting tendency of the substance on the right—its reaction tendency is *proportional* to its molecular concentration and the latter is written $[H_2O$ vapor$]$.

To obtain the actual value of the reaction tendency, we must multiply this expression by its proportionality constant. Denoting the latter by $K$, we obtain the following value for the reacting tendency of the vapor:

$$K\times[H_2O \text{ vapor}]$$

Finally, we note that, *at equilibrium*, the two opposing tendencies are equal; hence we have—

$$k=K\times[H_2O \text{ vapor}]$$

or $[H_2O$ vapor$] = k/K =$ a fixed value, which means that, at constant temperature the concentration of the vapor has a fixed value —which accords with the facts.

*Exercise:* Write out the above argument applied to the second example of equilibrium, using "$KNO_3$ solid" and "$KNO_3$ dissolved" respectively, and ignoring the solvent.

### 7. The Law of Mass Action Applied to the Equilibrium Between Iron Oxide, Hydrogen, Iron and Steam.

Let us now turn our attention to the example presented in this chapter, the equation for which is:

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O.$$

Here we have to deal with the cooperative action of two substances in each mixture, and to apply the mass law we must *multiply* together the concentrations of all the substances taking part in the action, because if a quantity is proportional to several distinct numbers, then it is proportional to their *product.*

We will consider the mixture on the left side first. Since the activity of the solid (iron oxide) is fixed, it has a certain value which we will represent by $a$. The hydrogen has four distinct molecules involved in the reaction,—hence it exerts its influence *four* times or acts as *four distinct* substances, and its effect is proportional to $[H_2]\times[H_2]\times[H_2]\times[H_2]$ or $[H_2]^4$. The combined activity of the solid and the hydrogen is *proportional* to: $a \times [H_2]^4$; hence it is *equal* to *this value multiplied by the proportionality* constant. The latter we shall designate by $k$; hence the combined activity is equal to $k\times a\times[H_2]^4$.

In the same way, we obtain, for the value of the reaction tendency of the mixture of the right side, the expression $K\times b\times[H_2O \text{ vapor}]^4$, $K$ being the proportionality constant of this mixture and $b$ the fixed reactivity of the solid iron.

At equilibrium, the two reaction tendencies are equal; hence we have

$k\times a\times[H_2]^4 = K\times b\times[H_2O \text{ vapor}]^4$. On simplifying, we obtain

$$\frac{[H_2]^4}{[H_2O \text{ vapor}]^4} = \frac{Kb}{ka} = \text{a } \textit{fixed} \text{ value}$$

$$\text{or } \frac{[H_2]}{[H_2O \text{ vapor}]} = \sqrt[4]{\frac{Kb}{ka}} = \text{another } \textit{fixed} \text{ value.}$$

This equation shows that, at equilibrium at any particular temperature, the ratio of the concentration of the hydrogen to that of the steam is always a certain value. The value of this ratio was experimentally found to be

0.69 at 900° C.
0.78 at 1025° C.
0.86 at 1150° C.

We are now prepared to answer the question asked at the end of Art. 5 above.

The reacting tendency of either pair of the above reacting substances,—i. e., iron and steam, or iron oxide and hydrogen—changes with the concentration of the gaseous member of this pair, because the reacting tendency of the pair is equal to the product of the concentration of the solid and the concentration of the gas, and since the concentration of the solid is constant, the value of the product changes with the concentration of the gas.

When one of the original sets of substances in this experiment—say, *iron and steam*—start to react in the "closed vessel," there will be a decrease in their quantities with a consequent decrease in the concentration of the steam, and hence a decrease in the reacting tendencies of this pair of substances. Furthermore, the iron oxide and hydrogen produced by the reaction will be present in small amounts at first, and although the iron oxide will be present in its usual concentration from the start, yet the hydrogen will be present in very small concentration at first, and hence the reaction tendency of this pair of substances will be only slight. But, as the reaction proceeds, their amounts and hence their reaction tendency will increase steadily, while that of the original substances will decrease steadily: finally, the two become equal, and then all reaction ceases.

In conclusion, we wish to show the application of the foregoing to reactions in general. Nearly all reactions that the student will meet are incomplete reactions just like the above. Those reactions which *appear* to be complete differ from the above illustration only in not reaching their equilibrium conditions until one or more of the original reacting substances are practically exhausted; but, in reality, slight amounts of them (at least) always remain to help maintain the equilibrium.

### Questions on Chapter V.

1. With its temperature kept constant, is the chemical effect or tendency to reaction of a chemically reacting substance constant, or variable, and, if the latter, what is the amount of variation proportional to?

2. Describe briefly but definitely how Dumas and others made the earliest determination of the ratio by weight in which hydrogen and oxygen combine to form water.

3. The velocity of a chemical change is the amount of its products formed per second. A little reflection will show that in any reaction mixture kept at constant temperature the velocity,

and the force which impels the change, are proportional to each other (because the resistance or "friction" remains constant!); hence the velocity may be substituted for the reaction tendency or activity in the whole discussion of Art. 6. *Repeat the whole argument of Art.* 6 *with this substitution.* Equilibrium will then appear to be two opposed reactions taking place with equal rapidity: this is the kinetic theory view of equilibrium. It is immaterial which view we take;—that of equilibrium being a balancing of equal opposing forces, or its being due to opposed changes taking place with equal rapidity,—the relations and results obtained are the same.

## CHAPTER VI.

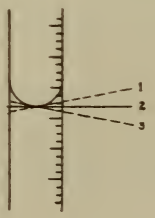
## ACIDS, BASES, AND SALTS.

### 1. Introduction.

Such substances as sulphuric acid, hydrochloric acid, acetic acid (vinegar), etc., have been designated as acids by all men for many years; while lime, caustic soda, iron oxide (iron rust), etc., have been designated as *bases* by all men for many years. When any one acid and any one base are brought in contact they react in practically the same manner as any other acid with any other base,—in a manner which may be expressed briefly by saying that *an acid and a base react to form a salt and water.* Since each non-metallic element is the essential component of at least one acid, and each metallic element is the essential component of at least one base, and since all acids react with *all* bases (to form the corresponding salt—and water), it is clear that the terms *acid, base,* and *salt* designate the three largest classes of compounds, and that the reaction between acids and bases is probably the most fundamental, general reaction with which we have to deal. For this reason it is taken up early in the course and the facts connected with its are presented at length.

### 2. Various Examples of the Interaction of an Acid with a Base.

**Experiment** (a).—(Two students may work together.) Secure two clean burettes, put dilute hydrochloric acid into one and sodium hydroxide solution into the other. Fill each "nozzle" *full* of the solution. Then fill the burettes to the "zero" mark (for reading the burette, see accompanying figure). Clamp the burettes in position for use. From the bu-




Meniscus - Correct reading along line 2

rette which contains sodium hydroxide, pour exactly 25 c.c. into a medium sized beaker, add 2 drops of methyl orange solution to it, secure a small stirring rod, and then, while constantly stirring the liquid in the beaker, add hydrochloric acid from the other burette until one drop "has just turned" the color of the "indicator" from yellow to pink. Ascertain how

much of the acid solution was used and record the amount. If the burettes need refilling, they should be refilled from the same supply from which they were filled at first in order that the solutions used throughout this experiment be of the same strength. This determination of the amount of one solution which is required for complete reaction with another is called "titration."

Is there any heat given out during the reaction?

Taste the "neutralized" solution; take a little of each of the original solutions, dilute them largely and then taste them cautiously.

Pour the neutralized solution into a clean small porcelain dish, and concentrate it by evaporation over a piece of asbestos board until crystals are formed. If hydrochloric acid were thus evaporated, no residue would be obtained because this substance is a gas; and if the sodium hydroxide were evaporated, a whole solid of totally different appearance would be obtained.

Enter in your note book any indications that the original substances have reacted.

The weight relations in the reaction just presented are:

$$NaOH+HCl=NaCl+H_2O.$$

To ascertain that the ratio between the reacting substances is the same irrespective of the *total* amounts taken, repeat the titration by starting with only 5 c.c. of the sodium hydroxide solution, and again by starting with 10 c.c.

If instead of a soluble base, such as sodium hydroxide, an insoluble base is treated with an acid, a "color indicator" cannot serve to indicate the "end-point" of the reaction because the indicator is affected only by *solutions* of bases or acids. Hence in treating an insoluble base we make use of other indications to recognize when all of the acid has been used up. How this may be done is shown in the next experiment.

**Experiment** (b).—Into a medium sized beaker, put about 25 c.c. of dilute sulphuric acid, add about an equal volume of water, heat the mixture till it boils, and then add powdered copper oxide in small amounts at a time until some of it remains undissolved. Filter off the excess of copper oxide, evaporate the liquid to a small fraction of its original volume, and set it aside to cool. If it has been concentrated sufficiently, crystals of copper sulphate ($CuSO_4,5H_2O$) will appear as the liquid cools.

Since copper oxide itself is insoluble in water, and since the presence of the acid in water does not change the physical properties of the liquid and hence does not enable the water to dissolve the unchanged copper oxide, it follows that the latter must have been changed by the acid into a soluble substance: hence the fact that the powder disappears indicates that the acid is reacting with it. When the acid has been consumed through this reaction the powder ceases to disappear.

Proceeding in a manner similar to the procedure for copper oxide, try magnesium oxide with hydrochloric acid, and lead oxide with nitric acid. Be careful not to add more than a very slight excess of the base, and evaporate these solutions to smaller bulk than the solution of copper sulphate because the magnesium chloride and the lead nitrate here produced are more soluble than copper sulphate.

### 3. Definition of the Terms: Acid, Base, Salt.

Any substance is an acid (or a base) if it reacts with another substance universally recognized as a base (or as an acid, respec-

tively), to form a salt and water in a manner similar to that shown in the preceding examples.

#### 4. The Essential Components of Acids, Bases, and Salts.

Acids are compounds of hydrogen and an "acid radical" which may be either simple, as in HCl, or complex, as in $HNO_3$.

Bases are compounds of a metal (or its equivalent) and oxygen or the hydroxyl radical (OH).

Salts are compounds of a metal and of an acid radical.

All of them are *binary* compounds essentially,—that is, they are composed of two kinds of parts only. Thus potassium nitrate, $KNO_3$, is essentially a compound of potassium (K) and the nitric acid radical ($NO_3$). It is less in conformity with its behavior to consider it as made up of the three separate elements which appear to enter into its composition. The two constituent parts of which acids, bases, and salts are thus directly compounded are called *ions*. The ions formed by metals and "acid" hydrogen are more particularly called cations or positive ions, and the ions formed by hydroxyl or acid radicals are called *anions* or negative ions. These names are derived from the names of the poles of an electrolytic cell, *cathode* and *anode,* since ions were first clearly recognized in connection with the phenomenon of electrolysis. The mutual action of acids, bases, and salts in solution consists of an exchange of these parts or ions during which exchanges the ions remain integral.

#### 5. The Relation Between the Numbers of Atoms and Radicals (Ions) Which Appear as Replacing Each Other in Compounds or as Combining With Each Other to Form Compounds.

When we compare the formulæ of any of the metal oxides above—for example, of sodium oxide, $Na_2O$—with the formula for water, $H_2O$, it appears to us that the sodium oxide contains two sodium atoms where the water contains two hydrogen atoms,—or in other words, each Na has replaced an H. When we compare the formula for common salt, NaCl, with the formula for hydrochloric acid, HCl, it appears to us again that one Na occupies the place of one H, or takes the place of the latter. In other words, it appears that one sodium atom always takes the place of one hydrogen atom. This is true for all compounds in which sodium atoms appear to have taken the place of hydrogen atoms.

A comparison of the formula for water with the formula of the oxide of another metal—CaO—shows that one calcium atom takes the place of two hydrogen atoms: this apparent replacement of the two H's by Ca is also shown by the formulæ of all other compounds in which Ca appears in place of H.

Similarly we could show that every other metal atom displaces a definite number of hydrogen atoms.

Looked at from another standpoint, the formulæ of the various compounds show another similar relation. When we compare the formula for hydrochloric acid, HCl, with the formula for water, $H_2O$, we note that Cl holds only one H combined with it, while O holds two H's combined with it. When we compare the sodium compounds of these elements, NaCl and $Na_2O$, we find again that the oxygen atom holds twice as many atoms combined with itself as the chlorine atom holds combined with itself. In other words, the power of the oxygen atom to hold other atoms combined with itself is always twice as great as the power of the chlorine atom to hold other atoms combined to itself. Similarly we could show that other atoms or radicals exhibit a definite combining power corresponding to the number of hydrogen atoms they could combine with.

On account of this constancy of the number of atoms or radicals which an element or radical appears to replace or combine with, we are able to figure out the formulæ of the salts that will be formed from the basic oxide and the acids above. This requires merely the calculation of the proper number of metal atoms and of acid radicals which should be put together. For the purpose of calculating the numbers of these parts which belong together, chemists express the combining or the replacing power of atoms and radicals in terms of the number of H atoms which an element or radical can combine with or which it may replace: *this number of H's which an element or radical can combine with or may take the place of is called its valence.* Thus the valence of Na is one, of Ca is two, of O is two, of Cl is one, etc.

The formulæ for the salts are obtained by placing together as many metal atoms and as many acid radicals, respectively, as are necessary to make the sum of the valences from all the metal atoms equal to the sum of the valences from all the acid radicals. Thus for aluminium sulphate we proceed thus: we take the least common multiple of the valences of Al and $SO_4$, which is $2\times3=6$; then we ascertain the number of Al atoms which will give a total valence of 6—that is, 2Al—and we ascertain the number of $SO_4$ radicals required to give the same total valence of six—that is, $3SO_4$, and we write down the symbols side by side as shown here—$Al_2(SO_4)_3$, the two and three are written as subscripts because they refer only to a particular part of the symbol.

### 6. Exercise on Formulae of Acids and Bases and on Reactions Between Them.

To give the student facility in the use of symbols, formulæ and equations, the following exercise and directions are here included. Each part—*a*, *b*, *c*, or *d*,—should be done thoroughly

*before* beginning the next. Failure to observe this precaution will produce confusion.

(a) Commit to memory the formulae of the following bases and acids:

Bases—

| | |
|---|---|
| Sodium oxide | $Na_2O$ |
| Potassium oxide | $K_2O$ |
| Calcium oxide | $CaO$ |
| Copper oxide | $CuO$ |
| Magnesium oxide | $MgO$ |
| Zinc oxide | $ZnO$ |
| Iron (ferric) oxide | $Fe_2O_3$ |
| Aluminium oxide | $Al_2O_3$ |
| Lead oxide | $PbO$ |

Acids—

| Name | Formula | Name of Salt Formed |
|---|---|---|
| Carbonic acid | $H_2CO_3$ | Carbonate |
| Sulphuric acid | $H_2SO_4$ | Sulphate |
| Nitric acid | $HNO_3$ | Nitrate |
| Phosphoric acid | $H_3PO_4$ | Phosphate |
| Acetic acid | $H(C_2H_3O_2)$ | Acetate |

Note the relation between the terminations of the names of the acids and of their salts.

(b) Learn to recognize the valences of the metal atoms and of the acid radicals given in the compounds under (a).

(c) Figure out the formulae of the forty-five salts that may be formed from the nine bases and five acids above: do not attempt to write equations in this connection.

(d) Express by equations the reaction between all the acids and bases above. To do this put down first the formulae of the acid and base on the left-hand side of the equation and of the salt and water on the right-hand side, e. g.,

$$CaO+H_3PO_4=Ca_3(PO_4)_2+H_2O$$

Next, balance the equation without changing the formulae of any one of the substances: that is, add coefficients only. Thus, in the examples above, add the coefficients which give the following equation:

$$3CaO+2H_3PO_4=Ca_3(PO_4)_2+3H_2O$$

In this reaction we have two substances—each of which is composed of two parts—forming two new substances simply by an interchange of parts. In general, the change may be represented as follows: $AB+CD=AD+CB$. It must be observed, however, that in their recombination the four combine in accord-

ance with their valences. Reactions of this general form are known as *metathetical reactions.*

While thus learning to write equations, we must not come to the conclusion that we are learning to figure out what would take place. We can never figure out what takes place; that must be ascertained by actual measurement with the substances concerned. But the results of such measurements may be collected and expressed in a brief statement, and the information with reference to the mutual actions of acids and bases is conveyed in the statement,—*acids and bases react to form salts and water.* The object of the foregoing exercise is to show the student how to apply the general statement to special examples.

**7. The Solubilities of the Common Acids, Bases, and Salts.**

NOTE.—Accurately speaking, there are no really insoluble substances. The term "insoluble" is used here to designate substances which are so slightly soluble that their solubility is not ordinarily appreciable. Yet, under certain conditions, the dissolved portions of "insoluble" substances are noticeable.

*Acids:* All common acids except two are soluble in water, and hence affect "color" indicators and have a sour taste. The *insoluble* acids are silicic acid, $H_2SiO_3$, and arsenious acid, $HAsO_2$.

*Bases:* All common bases are insoluble except:

Ammonium hydroxide, $NH_4OH$
Potassium hydroxide, $KOH$
Sodium hydroxide, $NaOH$
Barium hydroxide, $Ba(OH)_2$
Strontium hydroxide, $Sr(OH)_2$
Calcium hydroxide, $Ca(OH)_2$

Calcium hydroxide is only slightly soluble. Naturally, only the soluble bases affect "color" indicators and the taste.

*Salts:* The *common* salts have the following solubilities:

All *common* salts of sodium, potassium, and ammonium are extensively soluble in water.

All *silver* salts are insoluble in water except silver nitrate, silver acetate, and silver sulphate. The last two are only sparingly soluble.

The *nitrates* and *acetates* of all metals are extensively soluble in water. Silver acetate is only moderately soluble.

The *sulphates* of lead, barium, and strontium are insoluble; calcium sulphate, mercurous sulphate, and silver sulphate are slightly soluble; and all other sulphates are extensively soluble.

The *chlorides* of silver and mercurous mercury are insoluble; mercuric chloride is moderately soluble; lead chloride is slightly soluble in *cold* water, but extensively soluble in *hot* water; and all other chlorides are very soluble.

The normal *carbonates* and *phosphates* of all metals are insolu-

ble, except those of sodium, potassium, and ammonium. (All acid phosphates and acid-carbonates are soluble.)

*These solubilities should be committed to memory.*

The alkali-metals are the elements of Group 1a of the Periodic System:—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and caesium (Cs). They are strikingly alike in the following properties:

They have the greatest tendency of all metals to change from free metal to compound, and this tendency increases with their atomic weights from Li to Cs; their hydroxides are all very soluble in water, they are extensively ionized (see next chapter), and hence they are said to be "strong bases"; nearly all of their salts are very soluble; they are monovalent in all of their compounds.

The alkaline-earth metals are the elements of Group 2a of the Periodic System:—glucinum (Gl), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

The hydroxide of glucinum is practically insoluble, and only feebly basic. The hydroxide of barium is quite soluble and a strong base:—the hydroxides of the intervening metals have intermediate properties, in the order of their atomic weights.

The tendency of these metals, to change to compounds is next in strength to the tendencies shown by the alkali metals.

The alkaline-earth metals are all bivalent in their compounds.

### 8. An Illustration of the Influence of Solubility Upon Chemical Reactions in Solutions.

The solubilities of the substances is one of the largest factors which determine whether or not metathetical reaction will take place. Thus even in the reaction between a base and an acid, for which there is always a decided tendency, insolubility of the salt formed will retard the reaction and may prevent it practically entirely. The following experimental procedure serves to show this. The experiment is an excellent one to develop chemical notions:

**Experiment.**—Put into each of three test-tubes a pinch of zinc oxide, and add to one just enough dilute HCl so that when the mixture is stirred and warmed the zinc oxide dissolves. Treat the second portion of zinc oxide with $HNO_3$, and the third with dilute $H_2SO_4$. In the same way try calcium oxide (or hydroxide), and lead oxide. Do you observe any relation between the solubilities of the salts that are, or should be, formed, and the rate at which reaction takes place? To ascertain this relation, tabulate your results in five vertical columns, headed, respectively:

| Base Used | Acid Used | Salt to be Formed | Solubility of this Salt | Observed Rate of Change |
|---|---|---|---|---|

When a "slightly soluble" salt is to be formed, the *tendency* to reaction between the acid and the base is, in general, just as great

as in any other example, but the first portions of the insoluble salt formed remain as a cover on the outside of each lump of oxide and hinder the access of the acid to the inner, unchanged portions of the lumps of oxide, and thus retard the progress of the reaction.

### 9. The Hydration of Oxides.

In Chapter I it was shown that the oxides of many elements *hydrate* on contact with water. It is intended to state here the most noteworthy facts concerning this hydration of oxides.

THE HYDRATION OF METAL OXIDES (BASES).—Nearly all metal oxides exist also in the hydrated form—as hydroxides—*but only those oxides whose hydroxides are soluble in water react on contact with water to form hydroxides.* None of the insoluble oxides *hydrate* themselves when in contact with water.

**Experiment** (a).—The hydration of calcium oxide may serve to illustrate the foregoing statements. Treat a few small lumps of fresh calcium oxide with a small quantity of water, stirring, or perhaps heating the mixture even, until the lumps crumble to a fine powder and all the water disappears.

What has become of the water? Has enough of it been vaporized to account for the loss in that way? Has the lime taken it up as a sponge takes up water? Make a special trial to decide this last point. Evidently the water has disappeared and is no longer to be found in its ordinary physical form. If this experiment were done with due precaution, and the quicklime and the water taken up were both weighed, it would be found that the two substances are in the proportion expressed by $1CaO:1H_2O$. The formula for calcium hydroxide is written $Ca(OH)_2$ to indicate the ions it forms in solution. It may also be written $CaO,H_2O$. The latter form shows the two oxides from which the compound is formed by simple combination. Formulæ written in this manner are known as "dualistic" formulæ.

**Experiment** (b).—Hydration does not affect the behavior which metallic oxides exhibit towards acids. To show this, heat a small portion of hydrated ferric oxide in a test-tube to drive off practically all of the water of hydration, this substance being one of the hydroxides which upon heating will dissociate into water and oxide. Treat the resulting oxide, when cool, with hydrochloric acid. That an action takes place is seen from the fact that the powder, which itself is insoluble, dissolves under these conditions. Now treat a portion of the original ferric hydroxide similarly with hydrochloric acid. No difference in behavior will be noticeable.

### 10. The Formulae of the Basic Hydroxides and Their Relation to the Formulae of the Corresponding Oxides.

The basic hydroxides have usually a composition which is expressed by coupling as many hydroxyl (OH) radicals to the symbol

of a metal as the valence of the latter amounts to; e. g., $Al(OH)_3$. This is the maximum extent of hydration possible. By a loss of water, lower states of hydration are obtained; e. g., $AlO(OH)$; and by complete "dehydration" the oxide is naturally obtained.

*Exercise:* Write out the formulae of the hydroxides of all the metals in the list above committed to memory.

Express by equations the complete dehydration of all these hydroxides.

Express by equations the reaction between all these hydroxides and the acids given in Article 34 (a).

### 11. The Hydration of the Acid Oxides.

Just as hydroxides of metals—i. e., bases—are related through hydration to an oxide of a metal, so many oxy-acids are related by hydration to the oxide of a non-metal—an *anhydride*. Unlike the basic oxides, however, the acid oxides are not hydrated to any extent that may be expressed by a general rule. Hence it becomes necessary to learn the amount of hydration in each case. The following list collects all necessary details for a number of the common oxy-acids, and these facts and relations should be learned by the student:

| Name | Ion Formulae | Formulae of Anhydrides | Dualistic Formulae |
|---|---|---|---|
| Sulphurous acid | $H_2SO_3$ | $SO_2$ | $H_2O,SO_2$ |
| Sulphuric acid | $H_2SO_4$ | $SO_3$ | $H_2O,SO_3$ |
| Nitrous acid | $HNO_2$ | $N_2O_3$ | $H_2O,N_2O_3$ |
| Nitric acid | $HNO_3$ | $N_2O_5$ | $H_2O,N_2O_5$ |
| Phosphorous acid | $H_3PO_3$ | $P_2O_3$ | $3H_2O,P_2O_3$ |
| Phosphoric acid | $H_3PO_4$ | $P_2O_5$ | $3H_2O,P_2O_5$ |
| Carbonic acid | $H_2CO_3$ | $CO_2$ | $H_2O,CO_2$ |

NOTE.—Salts derived from sulphurous acid are called sulphites; from nitrous acid, nitrites.

Nearly all the common acids are soluble in water, and hence their anhydrides hydrate on contact with water.

**Experiment.**—To demonstrate the hydration of acid oxides, drop a little phosphorus pentoxide into water.

### 12. Acid Salts.

Salts in which all the replaceable H's of the acid have been exchanged for metal "atoms" are called *normal salts*. It is possible, however, to exchange only a part of the H's in acids having more than one H in the molecule; since such salts still contain replaceable H's, and on this account exhibit *acid* properties, they are called *acid-salts*.

The formation of acid-salts takes place in the following manner: When an acid such as phosphoric, $H_3PO_4$, separates into

its main constituent parts (ions), at first only one H separates, leaving the remainder intact as a monovalent ion $(H_2PO_4)^-$; and when the first portions of a base are added to a solution of such an acid, the reaction of neutralization takes place as though $H_3PO_4$ were a monovalent acid, the composition of the acid radical of which is $(H_2PO_4)^-$. Hence the aluminium salt would have the formula $Al(H_2PO_4)_3$.

NOTE.—The valences of positive ions are designated with plus signs—e. g., $H^+$, $Ca^{++}$, $Al^{+++}$; those of negative ions with minus signs—e. g., $Cl^-$, $SO_4^{--}$, $PO_4^{---}$.

After enough base has been added to neutralize all of the first set of H-ions, then the second H ionizes extensively and leaves the bivalent ion $(HPO_4)^{--}$.

Hence when the amount of the base added to the acid is double that needed to neutralize the first H's in all the molecules of the acid, then the acid reacts as though it were composed of two replaceable H's and the bivalent ion $(HPO_4)^{--}$. For example, the aluminium salt produced under such conditions would have the formula $Al_2(HPO_4)_3$.

After the second hydrogen atom has been neutralized, then the tendency to ionize the third hydrogen atom may become effective: the acid then reacts as though it were composed of three H's and the ion $(PO_4)^{---}$, and forms *normal* salts.

Of course if enough base is added all at once to neutralize more than one or two H's the reaction immediately proceeds to the corresponding extent. Thus if a drop of sulphuric acid is added to more than enough of sodium hydroxide solution to neutralize the acid completely, then the salt $Na_2SO_4$ is formed immediately; but when the procedure is reversed; that is, when a drop of sodium hydroxide solution is added to a great deal of sulphuric acid, then it will form only the acid salt $(Na(HSO_4))$.

The (experimental) formation of acid salts, with polybasic acids, depends only on the relative proportions of acid and base mixed.

### 13. The Actual Preparation of an Acid Salt in the Laboratory.

Secure a fresh solution of tartric acid, $H_2(C_4H_4O_6)$, containing about 150 grams per liter, and a solution of potassium hydroxide containing about 200 grams to the liter and fill two burettes with these solutions, respectively. Measure out 10 c.c. of potassium hydroxide solution into a small flask, add 15 c.c. of the tartaric acid solution measured from the other burette, then heat the mixture to the boiling point, add a drop or two of phenolphthalein solution and finish neutralizing it by adding more tartaric acid from its burette. Cool the mixture under a jet of tap-water and add to it as much tartaric acid again as was necesary to neutralize the potassium hydroxide. Crystals of potassium acid-tartrate will be formed, according to the equation—

$$K_2(C_4H_4O_6)+H_2(C_4H_4O_4)=2KH(C_4H_4O_6)$$

Next heat the mixture to boiling and add KOH slowly, with constant stirring until an amount approximately equal to the original has been

added. Note that the crystals dissolve as KOH is added. Explain what happens in each step and write the equations of the three reactions. Note that the second portion of potassium hydroxide used is equal to the first portion used. The composition of the crystals that separated from the solution is $(KH(C_4H_4O_6)$ and they are called potassium acid-tartrate, or potassium bitartrate. Give reasons for both names.

### Exercise on Chapter VI.

1. Figure out the formulae of the acid-sulphates or bisulphates of sodium.—of calcium.—of aluminium.

2. State whether or not it is theoretically possible to obtain acid-salts of the following acids: Nitric acid, carbonic acid, acetic acid?

3. To distinguish the *three* different phosphates from each other, we designate as primary phosphates those formed by replacing one *H;* as secondary, those formed by replacing two H's: and as tertiary those formed by replacing all three H's.

Write out the formulae of the three phosphates of calcium.

4. Write the formula (do not give equation) of the following compounds: sodium carbonate, potassium phosphate, magnesium chloride, calcium acetate, barium nitrate, copper phosphate, ferric sulphate, aluminium chloride, ferric phosphate and magnesium sulphate.

5. Write the equations for the hydration of the following oxides, and calculate the amounts of water required to hydrate 1 gram of each one of them: calcium oxide, sodium oxide, sulphur trioxide, phosphorus pentoxide.

6. (a) Explain the origin of the prefix *bi* in the term "sodium bicarbonate."

(b) Give the *ionic* and the *dualistic* formulae of the following substances:

Sulphuric acid.
Nitric acid.
Phosphoric acid.
Sodium hydroxide.
Aluminium hydroxide.

## CHAPTER VII.

## IONIZATION AND THE GENERAL RELATION BETWEEN DISSOLVED ACIDS, BASES, AND SALTS WHICH RESULTS IN METATHETICAL REACTION.

### 1. Electrical Conductivity.

If a conducting wire in an electric circuit is cut and the wire ends thus produced are immersed into an aqueous solution of any acid, base, or salt, the electric current will flow again through the circuit,—which shows that such solutions are conductors of electricity. The first experiment given below is intended to show that the conductivity of these solutions is due to electrically charged particles formed from the dissolved acids, bases or salts.

The circuit to be used in the following experiment is that passing through a small 110-volt electric light globe. In the absence of an electric light circuit, a suitable magneto electric generator should be secured (see footnote). Cut one of the two wires leading to the electric light. To the two open ends thus obtained attach covered copper wires (annunciator wire) of such length that they will extend into a beaker on the desk where the work is to be conducted. Remove the insulation for a length of two to three centimeters from the ends of these wires. Secure a piece of ordinary glass tubing about fifteen centimeters long, and slip one of these wires through it until the bared end extends beyond the glass tube; fasten the wire in the tube by driving a soft wooden taper as a wedge into the tube. Then place the bare end of the second wire parallel beside the one fastened in the glass tube, and fasten the second wire securely along the outside of the glass tube by wrapping some "insulating tape" around the two. With the bare ends adjusted parallel to each other and from three to five millimeters apart, this "apparatus" is ready for use. When not in use, the annunciator wires are to be disconnected from the "cut" ends of the electric light cord, and the latter connected with screw connectors to leave them ready for future use. Although the handling of these exposed wire ends is not dangerous to most people, yet it is advisable not to touch the bare wire ends with the fingers when the current is turned on. Care should also be taken to prevent their coming in contact with gas pipes, water pipes, or other direct connections with the ground.

(Note.—The special *magneto generator* made by the Central Scientific Co., Catalogue, 1914, No. 2276 (price $5.00), has been found suitable to be used in place of an electric light circuit for this work.)

When these ends are put into contact with different substances the lamp will light up with a brightness somewhat proportional

to their conductivity, and with very poor conductors (so-called non-conductors), the lamps will not light up at all.

**Experiment.**—Try the conductivity of different substances: a piece of wood, an iron nail, a lump of sugar, a mass of dry table salt, alcohol, distilled water, kerosene oil, etc.

For the purpose of comparing the conductivities of different solutions, the bare ends of the copper wire should be the same distance apart in all trials, and immersed to the same depth (e.g., the length of the "bared" portions). This must be done in order to involve in every trial the same length and cross section of the solution in the conducting of the current from one wire to the other.

Put distilled water into the beaker, try its conductivity, then add a pinch of some soluble salt, for example, common salt; stir the mixture with a glass rod, and try the conductivity of the resulting solution; it conducts well. Compare the conductivity of this solution with the conductivity of its components—water and dry salt. Pour out the solution and remove the remnants of this solution by rinsing the beaker with a little distilled water.

The result obtained above might lead to the conclusion that the property of electrical conducting is produced by mere dissolution. To ascertain that mere dissolution does not change a substance from a non-conductor to a conductor, try in the same manner the conductivity of an aqueous solution of sugar. This trial indicates that not all dissolved substances are conductors.

The question arises: will a substance like sodium chloride which, dissolved in water, forms a conducting solution,—will it form a conducting solution in *all* solvents? An indication for an answer to this question may be obtained by trying the conductivity of the same salt dissolved in 95 per cent alcohol. This solution conducts very poorly,—in fact, the conductivity of the alcohol is not appreciably increased by dissolving salt in it. Hence, it appears that the salt dissolved in water must have undergone some other change besides mere dissolution, which change has converted the solution into an electrical conductor. The same is equally true of all acids, bases, and salts.

### 2. The State in Which Acids, Bases, and Salts Exist in Aqueous Solutions.

A careful consideration of a large number of different experimental facts has led chemists to the conclusion that the particular change which occurs when acids, bases, and salts dissolve in water,—that this change consists of the separating of some of the molecules into distinct parts called *ions*,—each of which carries a definite number of electric charges, the number of which is the same as the valence number of the ion. Metal ions and hydrogen carry positive charges, while the non-metals, the acid radicals, and the hydroxyl (OH) ions carry negative charges. This "dissociation" takes place as follows: The metal atoms or the "acid" hydrogens give to the other parts with which they are associated in the molecules of acids, bases, and salts as *many* particles of negative electricity (called *electrons*) as their valence number amounts to. Thus when sodium chloride "ionizes," each Na gives *one* electron to the Cl from which it separates. The absence of this electron from the otherwise neutral Na is what is called a positive

electric charge, and the presence of this electron on the Cl is what is called a negative electric charge. Every ion has on it as many electric charges as its valence number amounts to,—thus Cu has two positive charges, $SO_4$ has two negative charges, etc. The presence of these charges is expressed by various means—in this book a positive charge is denoted by a plus mark placed at the upper right-hand corner of the symbol, and the negative charge by a minus sign placed as usual; e. g.: $Cu^{++}$, $Cl^{-}$, $K^{+}$, $SO_4^{--}$, $Al^{+++}$ or $Al^{3+}$, $PO_4^{---}$, or $PO_4^{3-}$, etc.

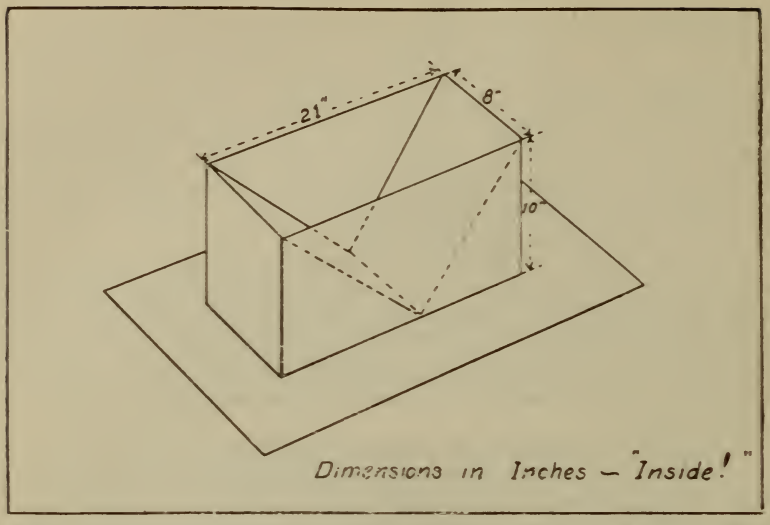
The composition of the ions was ascertained mainly by noting what parts of all acids, bases, and salts appear as displacing each other in forming new compounds. Thus it was observed that hydrogen is displaced by metals, OH is displaced by the various acid radicals, etc., and in the absence of any indications to the contrary it was concluded that these interchangeable parts are the distinct ions.

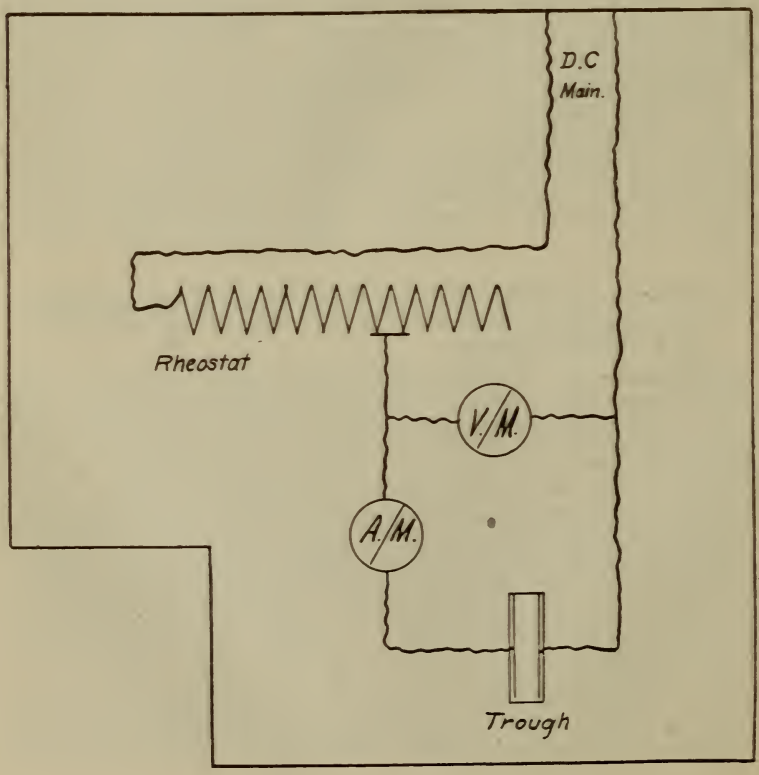
Not all of an acid, base, or salt in a solution is present in the form of ions: a part is present in the undissociated or combined part. This is due to the fact that the ions recombine when they meet. Thus it appears that there are two opposing actions possible in solutions of acids, bases, and salts,—ionization and recombination. These two opposing actions—or rather their tendencies to action—hold each other in equilibrium when a certain fraction of the dissolved substance is in the form of ions and the remainder in the undissociated form. In solutions of ordinary concentrations, the various acids, bases, and salts are ionized to greatly different extents; but all of them increase their ion-fraction on dilution, and hence, in extremely dilute solution, they are all entirely ionized.

### 3. Demonstration of the Increase of the Ion-Fraction with Dilution and the Determination of the Value of the Ion-Fraction of a Certain Solution.

**Experiment.**—(a) *The Conductivity Trough.*—Have a carpenter make a wooden vessel of the shape and dimensions given in the accompanying figure. Stout cypress or soft pine boards, at least 1¼ inches thick and perfectly smooth on both sides, are to be used. The vessel should be as nearly water tight as the carpenter can make it. It should then be thoroughly covered on the inside with melted paraffin to make it absolutely water tight, and in order that the boards may not take up any of the solutions poured into it. Now secure from a plumber or cornice maker a piece of fairly stiff sheet copper, at least 16 inches square. Cut it from one corner diagonally across to the opposite corner into two triangular pieces. If necessary, trim the short sides of the copper sheets to make them fit the triangular ends of the trough; but leave the excess of the plates at the top to be bent over the edge—to hold the plate in position close to the wood.

(b) *Preparing the Apparatus.*—Provide any suitable means for connecting the copper sheets to the wires of an electric circuit. Shake up about 200 grams of crystals of copper nitrate with about 50 c.c. of water until a *saturated solution* is obtained. Dilute 50 c.c. of this solution with


21"
8"
10"
Dimensions in Inches — "Inside!"


D.C
Main.
Rheostat
V/M.
A/M.
Trough

50 c.c. of water—thus securing a half-saturated solution—and pour these 100 c.c. of solution into the trough. Secure an ammeter of the total capacity of about one to two amperes; secure a voltmeter with a capacity of ten to fifteen volts; secure a source of direct electric current with a voltage of about ten volts (e. g., 6-8 dry cells); and secure a rheostat of about 30 ohms resistance and a current capacity of *at least* one ampere. Connect up the apparatus and the trough as shown in accompanying figure.

(c) *Operation.*—Turn on the current and adjust it with the rheostat until a current of about 0.1-0.2 amps. is passing. Note accurately both ammeter and voltmeter readings which are then shown by the instruments. In the following operations adjust the current so as to keep the voltage constant (at the value which has just been noted), and record in parallel columns the amount of the current that flows *after each* dilution of the solution. Dilute the solution by adding measured amounts of distilled water.

**4. Results.**

At the beginning, the increase in current will be relatively large with each addition of water; then it will become less until finally no further increase in current is obtained. The following results were obtained in a trial in which the current source was a battery of 5 storage cells (10 volts!) and the rheostat had a total resistance of 31 ohms. The voltage between the poles of the "trough" was maintained *constant* at 5 volts.

| Volume (c.c.) | Current (Amps.) | Ratio of Current to "Maximum" Current for *Whole* Amount of Salt. | Current per 100 c.c. Solution. |
|---|---|---|---|
| 100 | 0.16 | 0.24 | 0.16 |
| 200 | 0.31 | 0.47 | 0.155 |
| 400 | 0.41 | 0.62 | 0.102 |
| 800 | 0.49 | 0.74 | 0.061 |
| 1600 | 0.56 | 0.85 | 0.035 |
| 3200 | 0.62 | 0.94 | 0.019 |
| 6400 | 0.64 | 0.97 | 0.010 |
| 12800 | 0.65 | 0.98 | 0.005 |
| 14800 | 0.66 | 1.00 | 0.004 |
| 16800 | 0.66 | 1.00 | 0.003 |

The figures in the third column were obtained by dividing each value in the second column by the last or "maximum" value in the second column. They show that the conductivity of the half-saturated solution of salt used in the experiment is only 24 per cent of its maximum conductivity.

The figures in the fourth column should be carefully noted in contradistinction to the main result just mentioned: they are intended to show that the *dilute solution* is really a *poorer* conductor than a concentrated solution, even though a larger fraction of the dissolved salt is ionized in the dilute solution. This dif-

ference is due to the fact that in comparing the conductivities of *solutions*, we compare the conducting done by equal volumes; and the greater amount of salt per 100 c.c. in the more concentrated of two solutions gives, even with its smaller ion fraction, a greater amount of ions per 100 c.c.

### 5. Changes Accompanying the Passage of the Electric Current.

An electric battery cell, or a dynamo, may be looked upon as a "pump" which tends to push the "electric fluid" out at one of its poles, and draw it in at the other. The different wires and other apparatus connected with the cell or dynamo and through which the electric current flows may be looked upon as a series of pipes or tubes, which, together with the battery cell or dynamo, form a closed circuit in which the electric fluid is kept circulating by the pumping action of the cell or dynamo.

When, in the above experiment, the "trough" is connected so as to be a part of such an electric circuit, the electric fluid which arrives at one pole of the trough (the cathode) is used up in changing copper ions to copper metal, according to the equation,*

$$Cu^{++} + 2(-) = Cu^{\circ},$$

while, at the anode, an equal amount of electric fluid is regenerated through the reverse chemical change.

$$Cu^{\circ} = Cu^{++} + 2(-).$$

Thus it is seen that the electric fluid does not really *flow through* the solution in the trough as it does through the connecting wire, and the question arises: what happens in the solution while the electric current is flowing in the other parts of the circuit?

As stated above, copper ions are used up by the chemical action at the surface of the *cathode*; while new copper ions are produced at the surface of the anode. This leaves an excess of anions at the cathode, and an excess of cations at the anode. These unbalanced ions naturally oppose the continuation of the action, and hence tend to stop the flow of the electric current in the wire part of the electric circuit. They also attract oppositely charged ions (and repel ions with the same sign) in adjacent layers of the solution, and these layers act in turn upon the next layers, etc. As the result of these attractions and repulsions, all the cations are attracted and will move toward the cathode, and all the anions are attracted and will move toward the anode. As these ions arrive at the poles, they restore the electric neutrality there, and allow more electrons to flow through the wires, to the

*The exact significance of the symbols in this equation and the details of this action are presented on pages 160 and 161, which see.

cathode, and from the anode, respectively. Then more pole reactions will take place, and the same attendant operations will occur: this shows that the flowing of the electric current through the wire depends upon the rate at which the attracted ions arrive at the poles.

### 6. Cause of Increased Current Obtained on Diluting Solutions.

Having learned what is taking place in the solution while the current passes, we shall ascertain next why the current increases as the solution is diluted. Evidently the cause is something which increases the rate at which the ions arrive at the poles; hence we shall consider all the causes that can produce this effect.

(1) Force attracting (or repelling) the ions:—this is kept constant in our experiment by keeping the voltage between the poles constant.

(2) Mobility or friction that each kind of ion experiences as it glides through the solution: this is not changed by diluting the solution—as far as we know.

(3) Distance that the ions have to travel:—it is evident that each ion, when attracted to the pole, will take the shortest path to the pole,—i. e., they will travel from their original positions in lines perpendicular to the poles. But their "original" positions after each dilution are at the same perpendicular distance from the poles as before diluting, because the shape of the vessel allows the dissolved material to spread out *only parallel* to the poles. To make this clearer, let us assume that the solution is "cut into equal thin slices" parallel to the poles—both before and after dilution: the slices of diluted solution will be larger than those of the undiluted solution, yet each one will contain just as many ions as the other. Thus, we see that, on the whole, the ions remain throughout the experiment at the same perpendicular distances from the poles, and always have the same distances to travel.

Besides the force attracting the ions, the mobilities, and the distances they have to travel—all of which are maintained constant and hence do not bring about the increase of the electric current observed,—besides these there is only one other way to obtain this increase, and that is by an increase in the *total number* of free ions. This is the cause of the increase in current.

In order to account for the fact that a fixed amount of a salt can produce different amounts of ions according to the volume in which it is dissolved, a Swedish chemist, Swante Arrhenius, suggested the idea that *the maximum conductivity shown by a fixed amount of a salt in very large volumes* is due to *all* of it being in the form of ions, and the lesser conductivities it shows when confined in smaller volumes are due to the fact that only proportionate fractions of the fixed amount of salt are in the form of ions—

(provided the "mobility" of each kind of ions is the same at all dilutions). The fractions given in the third column of the table of results above state the fractional amounts of the salt which are ionized.

### 7. The Fractional Amounts Ionized in Common Solutions of Acids, Bases, and Salts.

**Experiment.**—Ascertain the conductivities of the following: Dilute hydrochloric acid; dilute acetic acid; dilute sodium hydroxide solution; dilute ammonia solution; sodium acetate solution; ammonium chloride solution; ammonium acetate solution.

These trials show that both acids and bases differ greatly in their fractional amounts ionized, while salts show no noticeable difference even though they are derived from acids and bases which differ greatly in their fractional amounts ionized (which trial shows this point about salts?).

The following general statements cover the fractional amounts ionized in all solutions of acids, bases, and salts. They should be committed to memory.

*Acids:* All *strong* acids (hydrochloric, nitric, and sulphuric) are highly ionized in aqueous solutions. All *weak* acids (phosphoric, acetic, sulphurous, carbonic, and hydrogen sulphide) are moderately to very slightly ionized.

*Bases:* All *strong* bases (all soluble bases except *ammonia*) are highly ionized. All *weak* bases (ammonia) are slightly ionized.

*Salts:* *Normal* salts are highly ionized (ferric sulphocyanate, $Fe(CNS)_3$, lead acetate $PbAc_2$, mercuric chloride $HgCl_2$, mercuric cyanide $Hg(CN)_2$, and the halides of cadmium are exceptions).

Acid salts ionize extensively into the metal ion and into the acid ion (e. g., $NaHCO_3$ ionizes extensively into $Na^+$ and $(HCO_3^-)$ ions).

*Water:* Water itself is very slightly ionized into $H^+$ and $OH^-$ ions. An idea of the number of ions in *pure* water can be gotten from the statement that in a ton of water there are only 0.0017 gram of $OH^-$ ions.

*Insoluble or Slightly Soluble Substances:* It should be noted that insoluble or slightly soluble substances produce or maintain only few ions in solution.

In the table below are given the values of the fractions ionized of some typical acids, bases and salts, together with values of the ionization of some acid radicals. This table is presented for reference only.

TABLE OF IONIZATION VALUES OF ACIDS, BASES, AND SALTS IN 0.1 N SOLUTIONS AT 18° C.

ACIDS

| | |
|---|---|
| Hydrochloric Acid—$HCl=H^+ + Cl^-$ | 92.00 |
| Nitric Acid—$HNO_3=H^+ + NO_3^-$ | 92.00 |
| Sulphuric Acid—$H_2SO_4=H^+ + HSO_4^-$ | 47.00 |
| Acid Sulphate ion—$HSO_4=H^+ + SO_4^{--}$ (37. per cent of 47) | 17.39 |
| Phosphoric Acid—$H_3PO_4=H^+ + H_2PO_4^-$ | 27.00 |
| Dihydrogen Phosphate ion—$H_2PO_4=H^+ + HPO_4^{--}$ | 0.14 |
| Monohydrogen Phosphate ion—$HPO_4=H^+ + PO_4^{---}$ | 0.0002 |
| Acetic Acid—$HAc=H^+ + Ac^-$ | 1.30 |
| Carbonic Acid—$H_2CO_3=H^+ + HCO_3^-$ | 0.17 |
| Acid Carbonate ion—$HCO_3^-=H^+ + CO_3^{--}$ | 0.01 |
| Hydrogen Sulfide—$H_2S=H^+ + HS^-$ | 0.07 |

BASES.

| | |
|---|---|
| Potassium Hydroxide—$KOH=K^+ + OH^-$ | 91.00 |
| Sodium Hydroxide—$NaOH=Na^+ + OH^-$ | 91.00 |
| Barium Hydroxide—$Ba(OH)_2=Ba^{++} + 2OH^-$ | 77.00 |
| *Barium Hydroxide—$Ba(OH)_2=Ba^{++} + 2OH^-$ | 92.00 |
| *Strontium Hydroxide—$Sr(OH)_2=Sr^{++} + 2OH^-$ | 93.00 |
| *Calcium Hydroxide—$Ca(OH)_2=Ca^{++} + 2OH^-$ | 90.00 |
| Ammonium Hydroxide—$NH_4OH=NH_4^+ + OH^-$ | 1.30 |

*These concentrations are 1/64 normal.

SALTS

| | |
|---|---|
| Potassium Chloride—$KCl=K^+ + Cl^-$ | 86.00 |
| Silver Nitrate—$AgNO_3=Ag^+NO_3^-$ | 86.00 |
| Sodium Acetate—$NaAc=Na^+ + Ac^-$ | 79.00 |
| Barium Chloride—$BaCl_2=Ba^{++} + 2Cl^-$ | 77.00 |
| Potassium Sulphate—$K_2SO_4=2K^+ + SO^{--}$ | 72.00 |
| Sodium Bicarbonate—$NaHCO_3=Na^+ + HCO_3^-$ | 78.00 |
| Sodium Phosphate—$Na_2HPO_4=2Na^+ + HPO_4^{--}$ | 73.00 |
| Cadmium Iodide—$CdI_2=Cd^{++} + 2I^-$ | 10.00 |
| Mercuric Chloride—$HgCl_2=Hg^{++} + 2Cl^-$ | 0.006 |

The *chemical activity* of acids, bases, and salts is not proportional to their *total* concentration, but is proportional to the concentration of *free* ions. This general fact is strikingly illustrated by the great difference in the rate of action, upon zinc, of the strong acids (hydrochloric, dilute sulphuric) as compared with the slow rate of action of weak acids (acetic, phosphoric). Test-tube trials of these actions should be made if the facts cannot be recalled readily from Chapter III by the student. Compare rates of reaction with ionization values from the above table.

### 8. Details of the Relations Between Dissolved Substances Which Undergo Metathetical Reactions.

Extensive study of the reactions between acids, bases, and salts has led to the following conclusions:

1. Anions and cations combine readily to form neutral mole-

cules and in any solution every possible combination of the anions with the cations present is formed.

2. The amount of any one combination formed depends upon the nature of this combination. If it has a great tendency to ionize, then it exerts a great force in opposition to the union of the ions, and the amount formed from its ions will be small, even if, to begin with, the solution contains many free ions of this combination; if the combination to be formed has a slight tendency to ionize, the extent to which the ions will combine will be great.

To illustrate the above: When a solution of an acid (HCl) has a solution of a base (NaOH) added to it, then the two cations ($H^+$ and $Na^+$) will, on meeting the anions ($Cl^-$ and $OH^-$), form the four combinations,—HCl, NaCl, NaOH, HOH. Of the first three compounds only small amounts can be formed because their tendencies to ionize are so great that small concentrations of these substances are enough to stop further combining. But the fourth substance has such a slight tendency to ionize that it does not prevent the uniting of its ions until the supply of either $H^+$ or $OH^-$ ions is practically exhausted.

It appears from the above that the only extensive change in this solution is the disappearance of the $H^+$ and $OH^-$ ions which form water according to the equation: $H^+ + OH^- = H_2O$.

The ordinary equation for the reaction between an acid and a base does not express this fact—that the reaction consists of the extensive combining of a pair of free ions; but it may be made to do this by the following modification:—express as free ions those substances present in greater part as free ions, and express by the ordinary formulæ those compounds which are present in greater part as undissociated substances. The equation for the reaction betwen sodium hydroxide and hydrochloric acid will thus be written:

$$Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O.$$

**9. Demonstration of the Disappearance of Ions in the Reaction Between an Acid and a Base.**

Secure three medium-sized beakers (300-400 c.c.), fill two with pure distilled water, add to one just enough dilute hydrochloric acid (a drop or two) to make it enough of an electrical conductor to allow the lamp in the conductivity apparatus to burn dimly; then add just enough sodium hydroxide solution to the other beaker of water to secure a solution of the *same* conductivity. Mix equal volumes of these solutions in the third beaker, and compare, by trial, the conductivity of the mixture with that of its separate components: the mixture will be found to have a much small conductivity.

If ions had not disappeared, the mixture would have shown the same conductivity as the solutions from which it was prepared. The lesser conductivity indicates a decrease in the number of ions and thus accords with the explanation of the reaction given above.

**10. The Fundamental Relation Which Brings About Metathetical Reaction.**

According to the Mass Law (see Chapter V, Art. 6), the combining tendency of $H^+$ with $OH^-$ ions to form $H_2O$ is *proportional to the expression:*

$$[H^+]\times[OH^-]$$

and it is *equal* to $k\times[H^+]\times[OH^-]$, k being the proportionality constant (or, in other words, $k$ is the value of the combining tendency when the contents of the braces have the value *one*).

The dissolving tendency of water is naturally a *constant* because it cannot vary its concentration. Let this constant value be denoted by $K$. Then, at equilibrium, we have

$$k\times[H^+]\times[OH^-]=K \text{ or } [H^+]\times[OH^-]=K/k=\text{a fixed value.}$$

With $H^+$ and $OH^-$ expressing numbers of gram-molecules per liter, the fixed value has been found to be $1/(10)^{14}$, and is known as the electrolytic dissociation constant for water.

If we mix a solution of sodium hydroxide with dilute hydrochloric acid, the value of the ion-product at the moment of mixing is naturally very much greater than this equilibrium value, $1/10^{14}$, and their combining tendency is proportionally greater. But the ionizing tendency of water is still the same, and only great enough to produce an ion product equal to $(1/10)^{14}$. Hence the combining tendency of the ions is much greater than the opposing ionizing tendency of the water, and therefore the ions combine.

To express this relation in symbols, we write:—

$$\underset{\text{in original mixture}}{[H^+]\times[OH^-]} > \underset{\text{from pure water}}{[H^+]\times[OH^-]}$$

This means that the *product* of the *concentrations* of the $H^+$ and $OH^-$ ions as *found in the original mixture just before reaction is* greater than the product of the concentrations of these ions as found in pure water. By multiplying these ion-products with their proportionality constant $k$, we obtain the relation of the *actual values* of the two opposing reaction tendencies—

$$\underset{\text{in original mixture}}{k\times[H^+]\times[OH^-]} > \underset{\text{from pure water}}{k\times[H^+]\times[OH^-]}$$

But the constant may be eliminated by dividing both sides by $k$; hence the expression above *without* the constant *expresses the relations of the two opposing reaction tendencies* just as well.

Naturally, reaction can take place only when the forward acting tendency is greater than the opposing tendency; and to ascer-

can whether or not reaction will take place. One need but ascertain the relation of the ion-products as shown in this example.

11. **Demonstration of the Fact That the Combining Tendency of a Pair of Ions is Always Proportional to the Product of Their Concentrations.**

**Experiment.**—Secure three clean 600 c.c. beakers, and by means of a burette measure out exactly 5 c.c. of the stock ferric chloride solution (10.5 gms. per liter) into beaker No. 1. Then with a graduate add 5 c.c. of dil. HCl and 400 c.c. distilled water. Measure out exactly 5 c.c. of the stock potassium sulphocyanide solution (10.5 gms. per liter) into the diluted solution, and stir the mixture. Keep this solution for comparison with No. 2 and No. 3.

Into beaker No. 2 put 5 c.c. of ferric chloride solution (burette), 5 c.c. of dil. HCl and 400 c.c. of distilled water. Then add potassium sulphocyanide solution from the burette until the color of the solution in beaker No. 2 is the same as in beaker No. 1. Note the amount of potassium sulphocyanide solution used.

Into beaker No. 3 place 5 c.c. of potassium sulphocyanide solution (burette), 5 c.c. of dil. HCl and 400 c.c. of distilled water. Then add ferric chloride solution from the burette until the color of the solution in beaker No. 3 is the same as in beakers No. 1 and 2. Note the amount of ferric chloride solution used.

None of the ions or ion-combinations possible in this mixture impart a deep color to it except the combination of the ferric ion with the sulphocyanate ion, which gives a blood red compound, ferric sulphocyanate. An exceedingly small quantity of this gives a deep red color to the solution. The equation for the formation of this combination from its ion is:—

$$Fe^{+++} + 3(CNS)^{-} = Fe(CNS)_3$$

Hence, according to the Mass Law, the combining tendency of these ions should be proportional to—

$$[Fe^{+++}] \times [CNS^{-}]^3$$

But a study of the behavior of polyvalent ions indicates that *each* valence behaves like a separate monovalent ion; hence the following equation really represents the change —

$$1.3Fe^{+++} + CNS^{-} \rightleftharpoons 1.3Fe(CNS)$$

and the combining tendency of the ion is *proportional* to

$$[1.3Fe^{+++}] \times [CNS]$$

or *equal* to $k$ times this expression, $k$ being the proportionality constant.

At equilibrium, each of the three beakers above contains the same quantity of ferric sulphocyanate (same color—same concentration) and hence all beakers contain as many ferric and sulphocyanate ions as are necessary to give the *same product*. Since

the quantity of the colored combination is relatively small, its formation used up a negligibly small quantity of ferric and sulphocyanate ions, and the quantities of ferric chloride and potassium sulphocyanate put into each beaker are proportional to the numbers of free ferric and free sulphocyanate ions present therein at equilibrium. Hence the *products of the numbers* of cubic centimeters of ferric chloride and potassium sulphocyanate put into all three beakers should be the same.

To test this, multiply the total number of cubic centimeters of ferric chloride by the number of cubic centimeters of potassium sulphocyanate used in each beaker; the product should be the same for all three beakers.

### 12. Other Illustrations of the Fundamental Relation in Metathetical Reactions.

The following examples are intended to show that the many reactions which occur between (a) two salts, (b) between a salt and an acid, or (c) between a salt and a base,—which consist merely of the forming of new ion combinations—that all of these so-called metathetical reactions take place on account of the same general relation between the original and the resulting substances which was shown to exist between the acid, the base, the salt and water in Art. 10. It should be noted that two substances do not necessarily react because they are mixed: they react only when the substances have the relations pointed out in Art. 10. The illustrations below include examples of each of the three possible combinations (a), (b), and (c) above, and they also include examples of non-reacting mixtures.

**Experiment.**—(a) Put a small lump of marble into a test-tube and add to it some hydrochloric acid which has been diluted to such an extent that only a moderately rapid effervescence occurs. Then add a pinch or two of crystals of sodium acetate; the marble serves only as an indicator and it shows that the hydrochloric acid is not present after the sodium acetate is added. Of course the experiment does not show *what* change has taken place, but it disposes the student favorably to receive the information *that a metathetical reaction has taken place.* We shall now consider what conditions bring about this reaction.

If a solution of sodium acetate is mixed with a solution of hydrochloric acid, the accidental meetings of the ions would form the two new combinations *acetic acid* and *sodium chloride.*

What is the extent of ionization of each of the four combinations in the mixture? Hence do the contents of the mixture at the moment of its preparation show the relation which is necessary to cause metathetical reaction? In other words, is either one of the following relations true?

1. $[Na^+]\times[Cl^-]$ in original mixture $>$ $[Na^+]\times[Cl^-]$ from its own solution

2. $[H^+]\times[C_2H_3O_2^-]$ in original mixture $>$ $[H^+]\times[C_2H_3O_2^-]$ from its own solution

Evidently one of them is true, hence the reaction takes place. The free hydrogen and acetions combine mostly to undissociated acetic acid molecules.

This lessening of the ions in the mixture may be demonstrated by means of conductivity experiments. For this purpose, dilute some hydrochloric acid until its conductivity is so slight that it allows the lamp to burn but dimly. Dilute a solution of sodium acetate to the same extent. Mix equal volumes of these solutions and try the conductivity of the mixture.

The equation for this metathetical reaction is:—

$$H^+ + Cl^- + Na^+ + (C_2H_3O_2)^- = Na^+ + Cl^- + H(C_2H_3O_2)$$

Since the only change that takes place in this mixture is the combination of the hydrogen ions and the acetions to form dissociated acetic acid, the change is completely represented by the equation:

$$H^- + (C_2H_3O_2)^- = H(C_2H_3O_2).$$

**Experiment.**—(b) Repeat the above test-tube trial with sodium nitrate in place of sodium acetate. Does this trial furnish any indication that a reaction has taken place? Consider the substances in this mixture just as the substances of the preceding mixture were considered in the preceding article, and try to reason out whether or not these two substances react.

Although a solution of any salt mixed with the solution of any other salt, acid or base would produce at least small amounts of two new compounds (e. g., $Na^+Cl^- + K^+NO_3^- = K^+Cl^- + Na^+NO_3^-$), yet such slight formations of new compounds are not ordinarily noticeable and hence are not considered to be reactions. Only the extensive formation of a combination of ions is spoken of as a reaction.

**Experiment.**—(c) Put a few c.c. of a concentrated solution of ammonium chloride into a test tube; note that it is practically free from any odor. Add some sodium hydroxide solution and note the strong odor of ammonia now emanating from the liquid. A metathetical reaction has taken place in the mixture. The formula for ammonium chloride is $NH_4Cl$: in this substance the radical $NH_4^+$ is a positive, monovalent ion like $Na^+$, and its combination with the $OH^-$ radical is called ammonium hydroxide or ammonia—formula $NH_4OH$. With this information write the equation for the reaction in the mixture just made.

Proceed to make conductivity trials as in Art. 9, using a weak solution of ammonium chloride, a weak solution of sodium hydroxide, and then the mixture of these two. Finally give an explanation of why the reaction takes place—following Art. 12, Experiment (a), as a model.

**Experiment.**—(d) Mix in a test-tube 1 c.c. of dilute silver nitrate solution with a few drops of dilute hydrochloric acid:—the white solid which is formed is the insolubie compound silver chloride, AgCl, which is formed by metathetical reaction. In this case we have *visible* evidence

that a reaction takes place. Write the ordinary equation for it, and also the equation which includes only the substances that actually change. Consider the relations of the substances and point out why reaction takes place. Then, by means of your knowledge of the solubilities and ionization relations of the substances in the following mixtures, predict whether or not their solutions will react when mixed:—

$AgNO_3 + NaCl$
$AgNO_3 + CaCl_2$
$Ag_2SO_4 + HCl$
$Ag_2SO_4 + NaCl$

Mix small amounts of solutions of each pair of substances and thus test your prediction.

Dilute a solution of silver nitrate until its conductivity is so small that the lamp will glow dimly. Secure two or more of the following chlorides and prepare similarly dilute solutions of them:—sodium chloride, potassium chloride, ammonium chloride, calcium chloride, magnesium chloride. Then mix equal volumes of a chloride and of silver nitrate solutions, and ascertain the conductivity of the mixture. The latter will be found to be perceptibly less than that of either constituent. State why.

**Experiment.**—(e) Mix in a test-tube one c.c. of a barium chloride solution with a few drops of dilute sulphuric acid: the white solid which appears is the insoluble compound, barium sulphate, $BaSO_4$, which is formed by metathetical reaction. In this case we have again visible evidence that a reaction takes place. Write the equation. Consider the relations of the substances and point out why reaction should take place. Then predict, from your knowledge of the solubilities and ionization relations of the substances in the following mixtures, whether or not their solutions react:—

$BaCl_2 + Na_2SO_4$
$BaCl_2 + MgSO_4$
$Ba(NO_3)_2 + H_2SO_4$
$Ba(NO_3)_2 + MgSO_4$.

Mix small amounts of solutions of these substances in test-tubes and thus test your predictions.

Make the usual conductivity trials with a dilute solution of barium chloride, with a dilute solution of a sulphate, and with a mixture of the two. State why the mixture should have a lesser conductivity than its separate components.

### 13. An Example of a Metathetical Reaction Brought About by Precipitating One Compound by Concentrating the Solution (and Another by Cooling).

Weigh out, on a platform scale "to the nearest gram," 25 grams of commercial sodium nitrate (Chile saltpeter) and 22 grams of commercial potassium chloride. Measure out 50 c.c. of distilled water, and heat this to boiling in a porcelain dish. While continuing to heat the dish with a medium-sized flame, add the sodium nitrate and stir the liquid with a glass rod until the crystals are dissolved. Then add the potassium chloride, and stir the mixture until this salt has dissolved. Increase the flame, and while steadily stirring the mixture, evaporate it rapidly to one half the bulk. Then allow the crystals to settle, decant the liquid as completely as possible into a small beaker, holding back the crystals, and finally press them with a spatula to get all the liquid possible out of them. They are crystals of common salt—sodium chloride.

Allow the liquid to cool thoroughly: the crystals which appear are composed of potassium nitrate. If necessary, the cooling of the liquid may be hastened by putting the solution into a small flask, and cooling its bulb with tap-water. However, the crystals obtained will be small. Finally, decant the liquid, dry the crystals between a few sheets of filter paper, and give them to the instructor in order to save this fairly valuable salt.

Look up the solubilities, at 100° C. and at 25°, respectively, of the four salts involved in this reaction: which salt will be precipitated first as the solution is concentrated? Note the relative amount of this same salt which will be precipitated on cooling the solution. Which salt will be precipitated extensively on cooling. Why?

### Questions on Chapter VII.

1. State whether or not a metathetical reaction will take place when solutions of the following pairs of substances are mixed, and point out which ion pair fulfills the fundamental condition that brings about the reaction. Then prepare in test-tubes small amounts of these mixtures. Do the results of these trials agree with your predictions?

(a) Sodium carbonate and sulphuric acid.
(b) Potassium sulphite and hydrochloric acid.
(c) Sodium carbonate and calcium chloride.
(d) Sodium chloride and acetic acid.
(e) Sodium chloride and copper sulphate.
(f) Sodium phosphate and copper nitrate.
(g) Sodium hydroxide and copper sulphate.

2. Considered in the light of the ion theory, what takes place in every metathetical reaction which may be looked upon as the real reaction taking place? Illustrate with three distinct examples from your own experience in this course.

3. State the extents of ionization of the common acids, bases and salts.

4. Given the apparatus for the experiment in Art. 3, properly connected for the beginning of the experiment:—state what is *done* in performing the experiment, and show how the larger current obtained in diluting the solution must be due to the fact that the fraction of the salt which is ionized increases with dilution. Show that all other possibilities for the increase are prevented by the conditions of the experiment.

5. If only 1 per cent of the acetic acid in a solution is in the form of ions, then, since only ions react, how does it happen that all of the acid will be neutralized when sufficient sodium hydroxide solution is added?

6. How does the per cent of ionization of acids, bases and salts change with dilution? Hence, does dilute hydrochloric acid contain more ions per c.c. than concentrated hydrochloric acid? Explain.

7. A liter of acetic acid solution contains, at equilibrium, 1 gram-molecule in the form of unionized molecules, and 0.0042 gram-ions of free $H^+$ ion and of $(C_2H_3O_2)^-$ ion, respectively: calculate the value of this "equilibrium" ion-product.

If hydrochloric acid gas is absorbed by this solution until the solution contains 0.1 gram-ions of free $H^+$ ions, approximately how many free acetions are left?

*Suggestion:* At equilibrium, the following relation exists:—

$$k \times [H^+] \times [C_2H_3O_2^-] = K \times [H(C_2H_3O_2]$$

$k$ and $K$ being the usual proportionality constants (see Chapter V, Art. 6). Dividing by $k$, we obtain

$$[H^+] \times [C_2H_3O_2^-] = K/k \times [H(C_2H_3O_2)]$$

$K$ and $k$ are fixed numbers; and since the amount of unionized acetic acid can be increased only from 1 to 1.0042 by the formation of more molecules through the union of the ions present, we may consider this number of unionized molecules constant,—hence all of the right side of the equation above is constant, and hence the left-hand side must be constant. This means that the ion-product must remain constant while the HCl gas is added. With this simplification, the problem is easily worked.

8. A solution of sodium acetate contains 1.1742 gram molecule per liter which we will assume to be completely ionized; a solution of hydrochloric acid contains 1.0001 gram molecules per liter—also assumed to be completely ionized. If one gram-molecule of unionized acetic acid is formed after the solutions are mixed, will the remaining ions (of $H^+$ and of $C_2H_3O_2^-$) remain free? Explain by calculating.

How much greater is the combining tendency of the $H^+$ and acetions in the above mixture just at the moment of mixing as compared with their combining tendency at equilibrium?

9. A certain solution of copper nitrate, when first put into the "trough" in Art. 3, has such a conductivity as to allow 0.43 amperes to pass. As the solution is diluted gradually, and the voltage is kept constant, the current increases to 0.68 amperes and remains at this value although the solution is diluted further. Calculate the fraction of the salt in the original solution which was in the form of free ions.

## CHAPTER VIII.

## THE PROPERTIES OF CARBON, SULPHUR, AMMONIA, THE HALOGENS, AND OF SOME OF THEIR IMPORTANT COMPOUNDS.

### 1. Introduction.

In the preceding chapters special attention was paid to the fundamental laws governing chemical changes; the necessary information and explanation of a large number of seemingly unrelated facts has been pointed out, in order that the study of future chemical facts might be approached with the idea of testing out the generalizations drawn as well as to increase our stock of chemical facts. This chapter, however, seeks primarily to enlarge the student's stock of special facts concerning elements and compounds, and, secondarily, to lead the student to the vantage point of viewing new facts in their relation to the older facts and in the application of the general principles stated. The chief properties of *carbon*, *sulphur*, the *hydrides* of these important compounds, and of ammonia will be presented in brief form. The facts presented are not related particularly to each other; they merely constitute a "working-kit" of necessary information.

### 2. The Properties of Carbon.

The diamond, graphite, lampblack, wood charcoal, and coke are substances which are distinct in appearance and in other physical properties such as hardness, electrical conductivity, specific gravity, etc. Yet all of them, under suitable conditions, combine with oxygen to form identical compounds, carbon dioxide; this reaction, in each case, takes place in the proportion by weight expressed in the equation—

$$C + O_2 = CO_2$$

Hence, these substances are merely different forms of the element carbon. However, they differ more or less extensively in their physical and chemical properties. Thus, the *diamond* form has a density of 3.5, is one of the hardest substances known, and will combine with oxygen only when surrounded with *pure* oxygen at a high temperature. *Graphite* is a shining black substance (the core of the "lead" pencil is an impure form of graphite), is soft, greasy to the touch, has a density of about 2.25 (compare this with the specific gravity of the diamond!), and it requires a high temperature for its ignition. It will be attacked slowly by the oxygen of the air if it is kept very hot. *Coke*, *charcoal*, and *lampblack* are so familiar to everybody that they do not need to be described. They begin to burn when heated to a moderately

high temperature and continue to burn. When the latter forms are heated without access to air to a very high temperature (3500° C.) they change to graphite.

**Experiment.**—(a) (In all experiments in this chapter, two students may work together.) Place a porcelain crucible on a clay covered triangle, tilting it so that it rests on its side. Put a small piece of charcoal into the crucible and heat it with a burner to ascertain how readily it burns. Then try a piece of graphite in the same manner. Although these two substances are identical in composition, yet they are quite different in properties. This is generally true of *allotropic* forms of a substance.

When equal weights of different forms of carbon are burned to carbon dioxide, they give out different amounts of heat, as expressed in the following equations:

$$C \text{ (lampblack)} + O_2 = CO_2 \text{ (gas)} + 97{,}650 \text{ cal.}$$
$$C \text{ (graphite)} + O_2 = CO_2 \text{ (gas)} + 94{,}810 \text{ cal.}$$

The difference between these amounts—i. e., 2,840 cal.—is the amount of heat given out when 1 C of lampblack (12 grams!) changes to 1 C of graphite. This change is similar to the change of liquid $H_2O$ to solid $H_2O$ (ice),—in which change 1.428 cal. are given out when 1 $H_2O$ (18 grams) changes.

Solid forms of the same element which differ in properties as these forms of carbon differ, are called *allotropic* forms of the element. Other elements which exist in several allotropic forms are sulphur, phosphorus, tin, etc.

At high temperatures, carbon combines directly with oxygen, hydrogen, nitrogen, sulphur and other elements. When air or oxygen is admitted sparingly to hot carbon, carbon monoxide—CO—is formed, but when this CO is mixed, hot, with more oxygen, or with substances which give up oxygen, then it changes to $CO_2$. When air is admitted sufficiently rapidly to hot carbon, it forms $CO_2$ immediately.

Many compounds of carbon and hydrogen exist, but only a few can be formed by direct contact of hydrogen with hot carbon. Combustible gases used in everyday life are composed largely of the compound $CH_4$—methane or marsh gas—or they contain CO—and some of them also contain hydrogen. It is such gases which in furnaces reduce metal oxide to free metals.

**Experiment.**—(b) Secure a piece or a stick of charcoal, and boil it in a concentrated solution of sodium carbonate. This treatment renders it practically non-combustible and the stick will thus serve as a suitable holder for the metal oxide.

Close the air holes of a Bunsen burner, and turn down the flame to one-third its usual height. Moisten the end of the charcoal stick and dip it into some powdered lead oxide, then hold it in the center of the flame:—globules of metallic lead will appear immediately.

Hot carbon combines directly with sulphur to form carbon bisulphide—$CS_2$—which is a clear liquid at ordinary temperatures.

Carbon does not combine directly with nitrogen, but a compound of carbon and nitrogen can be formed in an indirect way. It is known as *cyanogen,* and has the formula $(CN)_2$. It is an extremely poisonous gas. Compounds of cyanogen with metals or hydrogen are called cyanides. Of these, potassium cyanide—KCN—and prussic acid—HCN—are the best known. All cyanides are violent poisons.

Compounds of carbon and metals—called carbides—are familiar to everybody through calcium carbide, $CaC_2$. These carbides react on contact with water in a manner illustrated by the behavior of calcium carbide, which reacts according to this equation—

$$CaC_2+2H_2O=Ca(OH)_2=C_2H_2.$$

The compound $C_2H_2$ is the familiar substance called acetylene.

### 3. The Properties of Carbon Dioxide.

Carbon dioxide is formed whenever any combustible substance containing carbon is burned with free access of air. It is formed slowly during the decay of animal and vegetable matter. It occurs extensively in nature in the compound $CaCO_3$, which in its pure, crystalline form is known as *marble* or *calcite.* It also occurs in another crystalline form known as Aragonite or Dog Tooth Spar. Calcium carbonate is also the main component of limestone, of oyster shells, and of much other earthy material.

Carbon dioxide is a colorless, practically odorless gas. It is very heavy—about 1.5 times as heavy as air. It is fairly soluble in water: 1 volume of the gas dissolves in 1 volume of water at ordinary temperatures. It can be liquefied at 20° C. by compressing it under 56.3 atmospheres pressure.

Dissolved in water, it forms carbonic acid, $H_2CO_3$, and this acid forms normal carbonates with all bases except the bases of the trivalent ions (e. g., $Al^{+++}$ and $Fe^{+++}$). When heated, the carbonate of bivalent metals dissociate into carbon dioxide and the oxide of the metal,—as shown by the equation—

$$CaCO_3=CaO+CO_2.$$

The carbonate of Ca, Sr, and Ba dissociate much less extensively (or require a higher temperature) than the carbonates of the other bivalent metals. The carbonates of sodium and potassium—$Na_2CO_3$ and $K_2CO_3$—are stable even at high temperatures. The fact that the trivalent metals—Al and Fe—do not form carbonates indicates that the carbonates of these trivalent metals *dissociate completely* at ordinary atmospheric temperatures. Hence, when all the carbonates are arranged in the order of the temperatures required for their dissociation into metal oxide and carbon dioxide. they appear in the following order: $Na_2CO_3$ and $K_2CO_3$—

stable even at high temperatures; $CaCO_3$, $SrCO_3$, $BaCO_3$—dissociate at red heat; $ZnCO_3$, $CuCO_3$ and other bivalent metal carbonates—dissociate at temperatures below red heat; Al and Fe carbonate—dissociate at ordinary temperatures,—hence not formed at ordinary temperatures.

**Experiment.**—*The Preparation of Carbon Dioxide, and the Demonstration of Some of Its Common Properties.*

Fit up a 500 c.c. flask with a two-hole rubber stopper, a dropping funnel, and a delivery tube made by bending an ordinary glass tube, six inches long, near its mid-point to a right angle.

Secure another piece, twelve inches long, and bend it near one end to a right angle. Heat the ends of these tubes until the sharp edges have become rounded by slight fusion. Secure a two-inch piece of small—suitable—rubber tubing, and connect the short arm of this glass tube to the right-angle tube fitted in the stopper of the generating flask, and by means of this "conducting" tube pass the gas into the different vessels and substances as directed below.

Put into the flask a handful of powdered sodium carbonate (commercial washing soda). Moisten the salt with water and when ready to collect the gas, allow dilute sulphuric acid to drip into the flask from the dropping funnel. The substances first react metathetically to form $H_2CO_3$, and then this substance dehydrates:—

$$Na_2^+CO_3^{--} + H_2^+SO_4^{--} = Na_2^+SO_4^{--} + H_2CO_3$$
$$H_2CO_3 = H_2O + CO_2.$$

(a) Pass carbon dioxide into a little distilled water in a test-tube until the water is saturated (to determine the latter, close the test-tube with the thumb, shake it vigorously, and note whether or not a partial vacuum is created in the tube). Does the gas appear to be very soluble? Try blue litmus paper on this solution? What ions must be present to produce this change of color? Show by an equation how they were produced.

**Experiment.**—(b) Place a small piece of burning candle at the bottom of a large beaker and allow carbon dioxide to flow into the beaker until the flame is extinguished.

(c) Pass carbon dioxide downward into a dry, wide-mouth bottle (500 c.c.) while keeping the mouth of the bottle covered as well as possible with a piece of glass. Fasten some magnesium ribbon to the end of a piece of iron wire, ignite it, and lower it into the bottle: then try to find the carbon produced. Write the probable equation of this reaction. The burning of the magnesium in this gas is due to the high temperature created by the large amount of heat evolved from the reaction: this temperature is high enough to dissociate carbon dioxide into oxygen and CO, or into oxygen and carbon, and thus oxygen becomes available for the continuation of the combustion.

(d) Put about 50 c.c. of clear lime water into a small conical flask, allow carbon dioxide to pass into this solution until the precipitate first formed is redissolved, and then boil the solution.

### 4. Relation Between the Components of a Carbon Dioxide Solution.

A glance at the equations above and at the equation called for in (a) reveals the fact that in experiment (a) dioxide and water combine, while in the preparation of carbon dioxide they separate. Evidently this change is reversible; as in all such actions, so in

this, equilibrium is attained when the concentrations of the substances on the two sides of the equations bear a certain ratio to each other. If the relative concentration of $H_2CO_3$ is greater than this ratio, it breaks up into $CO_2+H_2O$ and if its relative concentration is less than this ratio, then $CO_2$ and $H_2O$ combine.

Every aqueous solution of carbon dioxide has, in addition to the equilibrium just pointed out, another equilibrium—namely, between the gas $CO_2$ and the dissolved $CO_2$; the gas dissolves in water or is liberated from the water until the concentration of the $CO_2$ gas above the water bears a certain ratio to the dissolved $CO_2$.

Hence a saturated aqueous solution of carbon dioxide presents the following equilibria:

(1) $CO_2$ (gas) $\rightleftarrows$ $CO_2$ (dissolved)

(2) $CO_2$ (dissolved) $+H_2O \rightleftarrows H_2CO_3$ (undissociated)

(3) $H_2CO_3$ (undissociated) $\rightleftarrows H^+ + HCO_3^-$

(4) $HCO_3^- \rightleftarrows H^+ + CO_3^{--}$

Thus, it is seen that there are *four* distinct equilibria existing in an aqueous solution of carbon dioxide. In connection with the last two equilibria, it should be recalled that all polybasic acids, such as $H_2CO_3$, $H_2S$, $H_2SO_4$, and $H_3PO_4$, have a much smaller tendency to ionize the *second* $H^+$ ion than the first $H^+$ ion, and a still smaller tendency to ionize any other $H^+$ ions present (as in $H_3PO_4$, for example). In this connection, look up the ionization values of polybasic acids given in the table in Chapter VII, Art. 7. It is on account of this lesser tendency to ionize that such acids form acid salts: with the first set of $H^+$ ions such acids act as stronger acids than with the second set.

By treatment with carbon dioxide dissolved in water, all carbonates are changed to bicarbonates or acid-carbonates. All bicarbonates are soluble in water,—and since the carbonates of the bivalent metals are insoluble, it follows that their conversion to bicarbonates is accompanied by the dissolving of these insoluble carbonates.

The bicarbonates of metals *other* than the alkalies are stable only in water charged with carbon dioxide. When the water loses this free, dissolved carbon dioxide, the bicarbonates change back to the normal salts according to the equation—

$$\begin{aligned} Ca(HCO_3)_2 &= CaCO_3 + H_2CO_3 \\ &= CaCO_3 + H_2O + CO_2. \end{aligned}$$

Hence, when such solutions are boiled, the dissolved solids separate from the solution.

Since natural water may secure carbon dioxide from the air, from decaying vegetable matter, etc., it frequently happens that natural water which has passed over limestone rocks contains large quantities of calcium bicarbonate, and when this water is boiled, calcium carbonate separates from the solution.

This deposition of calcium carbonate is often noticed when natural waters are boiled: the water becomes slightly opaque at first and afterwards clears up again when the insoluble calcium carbonate has settled. The bicarbonate of calcium (and of magnesium) in waters is known as "temporary hardness," due to the fact that it can be removed quite easily (a) by boiling or (b) by the addition of calcium hydroxide. The reaction of (a) is

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

and the reaction produced by the addition of $Ca(OH)_2$ is one of again changing the acid salt back to the normal salt, or

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

The bicarbonates of sodium, of potassium, and of ammonium do not dissociate but slightly at ordinary temperatures, and hence may be obtained outside of solution—as dry salts. However, their dissociating tendency increases markedly with the temperature, and they change to monocarbonates, according to the equation—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Sodium carbonate is known in commerce as sal soda, while the bicarbonate is known as cooking or baking soda. Sodium bicarbonate is less soluble than sodium carbonate.

### 5. The Fundamental Relation Which Brings About Metathetical Reactions in the Preparation of Carbon Dioxide.

The fundamental relation on account of which sodium carbonate solution and dilute sulphuric acid react is evidently—

$$\underset{\text{in original mixture}}{[H^-] \times [CO_3^{--}]} > \underset{\text{from saturated solution of } H_2CO_3}{[H^+] \times [CO_3^{--}]}$$

The expression on the right is small for two reasons: *first* because the solubility of carbonic acid is small, and, second, because this small amount of carbonic acid is only slightly ionized. It is hence not surprising that all carbonates—even so-called insoluble carbonates—react when mixed with any, even weak, acids. Hence in general it may be said that carbon dioxide may be prepared by taking any carbonate and treating it with any acid.

Make test-tube trials with several different acids and carbonates to demonstrate the above statement. Write all equations.

In practice, *sulphuric acid* would not be used with calcium carbonate. Why?

### 6. Carbon in Its Relation to the Other Members of Its Periodic Group.

Reference to the Periodic System (Chapter I, Art. 13) will reveal that carbon is in Group IV; associated with it are silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). The atomic weights range from 12 to 207 in the order given. Of this group, carbon is the typical element, being essentially non-metallic and forming an acid oxide—$CO_2$. Silicon approaches the metallic state more nearly, although its oxide—$SiO_2$—is still acidic. The other metals, Ge, Sn, and Pb become more metallic in nature and their oxides (of the general form $MO_2$) are basic in nature. $GeO_2$ is the transition oxide, having both acidic and basic properties.

Carbon and silicon exhibit a close relationship chemically: (a) they both exist in similar allotropic modifications; (b) they form similar hydrogen compounds, $CH_4$ and $SiH_4$; (c) they form similar oxides, $CO_2$ and $SiO_2$ (sand); and (d) they both form chloroform compounds, $CHCl_3$ and $SiHCl_3$.

It must be noted that carbon is dissimilar in certain respects from the other members of the group: (1) its oxides (CO and $CO_2$) are both gases, while the oxides of the other members are solids, and (2) it forms a much larger number of compounds with hydrogen, oxygen, nitrogen, etc., than any of the other members, constituting the large field of *organic chemistry* (see Chapters XIII and XIV).

The fact that the member of the first short period (carbon) differs more from the other members of its group (Si, Ge, Sn, Pb) than the latter differ among themselves,—this peculiarity appears also in all the other groups.

### 7. The Properties of Sulphur.

Sulphur is found in the earth in the form of the free element, and hence its preparation for commercial use consists merely of its separation from the earthy constituents mixed with it. It is also obtained commercially in heating iron pyrites—fool's gold—without access of air. Under these conditions, iron pyrites give up sulphur in the proportion by weight indicated by the equation—

$$3FeS_2 = Fe_3S_4 + 2S.$$

(Compare this equation with that for the decomposition of manganese dioxide at high temperatures!).

**Experiment.**—(a) Heat a little iron pyrites in a test-tube, and note the free sulphur formed.

Sulphur has an indefinite but low melting point. Its boiling

point is 444.6° C. In its chemical conduct it resembles oxygen in so far as it unites directly with metals, and it unites with hydrogen to form hydrogen sulphide, $H_2S$, and with carbon to form $CS_2$. A comparison of these two formulæ with $H_2O$ and $CO_2$, respectively, shows the similarity between the chemical properties of sulphur and oxygen.

**Experiment.**—(b) Bend a test-tube slightly at the mid-point, and put some sulphur into it; melt this and distill it, allowing it to drop into some water,—merely to show that it can be melted or distilled.

Mix intimately some very fine iron filings with an equal bulk of sulphur: put the mixture into a test-tube, and start it to reacting by heating the lower end of the tube until the glow started there proceeds practically of its own accord up through the mass. Show that a new substance has been formed; for this purpose add hydrochloric acid to small amounts of the original and of the resulting substances, and note any differences in the behavior of these mixtures. The iron and sulphur combined in the ratio expressed by FeS.

The common compounds of sulphur belong to the following three classes:

(1) Sulphides—related to or derived from $H_2S$.
(2) Sulphites—related to or derived from $H_2SO_3$ (or $SO_2$).
(3) Sulphates—related to or derived from $H_2SO_4$ (or $SO_3$).

The properties of the sulphides and of hydrogen sulphide will be studied farther on.

### 8. The Properties of Sulphur Dioxide.

Sulphur dioxide is the only product obtained whenever sulphur is burned in air or oxygen. It is a colorless gas, with an irritating odor. It is very heavy—about 2.2 times as heavy as air. It is very soluble in water: 1 volume of water dissolves 80 volumes of the gas. It is easilly liquefied because its boiling point is —10.1° C.

In its chemical behavior—i. e., in the formation and dissociation of sulphites and bisulphites, sulphur dioxide acts just as carbon dioxide does; but it differs from the latter in the fact that it has a tendency to take up more oxygen and change to $SO_3$. It shows this tendency even when it is dissolved in water—i. e., when it is in the form of $H_2SO_3$, it tends to form $H_2SO_4$. This tendency is the most notable property of sulphur dioxide. The manufacture of sulphuric acid makes use of this tendency of $SO_2$ to combine with oxygen.

The bleaching action of sulphur dioxide is due to the fact that it forms colorless compounds with the "carbonaceous" colors. Since these compounds dissociate again, the bleaching effect is not permanent.

**Experiment.**—(a) *The Preparation of Sulphur Dioxide and the Demonstration of Some of Its Properties.*

Prepare sulphur dioxide from a "mush" of bisulphite of soda and concentrated sulphuric acid, using the same apparatus as for carbon dioxide. As in the preparation of carbon dioxide, the substances first react metathetically to form $H_2SO_3$, and then this substance dehydrates—write the equations.

(b) *The Oxidation of Sulphur Dioxide by the Oxygen of the Air.*

Saturate 100 c.c. of water in a flask with the gas obtained in (a). Test the solution with litmus. Test a few drops of it by adding first a few drops of hydrochloric acid and then a few drops of barium chloride solution. Since barium sulphite is soluble in water, should there be any reaction? Put 20 c.c. of the same solution into a medium-sized flask and shake it vigorously so as to bring it extensively into contact with the oxygen of the air. Test again with hydrochloric acid and barium chloride. Note difference from preceding trial and explain, giving all equations.

(c) *The Oxidation of Sulphur Dioxide by Means of Oxidizers.*

Take another portion of the solution above and add to it potassium permanganate solution, a drop at a time, until no further change occurs. The color change shows that the permanganate is reduced:—that it gives up oxygen. Oxidize still another portion of the solution with a little concentrated nitric acid and note the brown fumes formed; these indicate that the nitric acid has been reduced. Test the resulting mixtures with barium chloride solution.

(d) *Bleaching Action of Sulphur Dioxide.*

Moisten some flowers and expose them to the sulphur dioxide in a flask: note that the color disappears.

State briefly the properties of sulphur dioxide which have thus been shown experimentally.

Point out the fundamental relations which brings about metathetical reaction in the preparation of sulphur dioxide by the method prescribed above.

When sulphur dioxide is absorbed in water, the same changes take place as with carbon dioxide. Write out the equations for the equilibria in this solution.

Write in proper order the equations for the reactions that take place when sulphur dioxide is absorbed in an excess of sodium hydroxide. If sulphur dioxide is added to the mixture after the sodium hydroxide has been neutralized, what reaction will take place then?

### 9. The Common Properties of Sulphuric Acid.

The manufacture of sulphuric acid should be demonstrated experimentaly on the lecture table.

**Experiment.**—Secure a clean, dry beaker of about 100 c.c. capacity, and a clean (dry!) burette with a glass stop cock. Fill this with concentrated sulphuric acid. (Be careful not to get any drop of this acid on the skin or on the clothing, but should this happen, remove it immediately by means of a large amount of water. Clothing should finally also be moistened with dilute ammonia.)

Weigh the beaker accurately and record the weight. Then pour into it

exactly 25 c.c. of sulphuric acid from the burette, and weigh the beaker and contents. Subtract the weight of the empty beaker from the latter weight, and divide the remainder by 25 c.c.:—the quotient is the specific gravity of the acid at room temperature. How much heavier than water is the acid?

Put the beaker with a wire gauze under it on a ring-stand in position to be heated. Secure a thermometer with a range of 200° C. or more, and suspend it in such a position that its bulb will be immersed in the acid in the beaker. Secure a large dish or tin pan, fill it with tap-water, and keep it in readiness to catch the acid in case the beaker breaks. Heat the acid slowly with a medium-size flame until the thermometer indicates about 190° C. Note that the acid does not boil even at that temperature. It is unprofitable, and somewhat dangerous to try to heat the acid to its boiling point (338° C.) and the above heating suffices to indicate that the boiling point of the acid is very high. Do not disturb the apparatus until the acid has cooled to 60° or below:—then pour it back into the supply bottle, and wash the apparatus with a large amount of water.

Fill the test-tube half full of distilled water, put it on the test-tube rack, and add to it *slowly* about one-eighth of a test-tube full of concentrated sulphuric acid. Note the large amount of heat liberated when sulphuric acid is diluted with (dissolved in!) water.

Whenever concentrated sulphuric acid and water are to be mixed, the acid should be poured *into the water:* the acid, being heavier than the water, sinks through the latter and thus helps to mix the liquids. With the reverse procedure, the water tends to float on top of the acid, and the great evolution of heat under the water may produce an "explosive" formation of steam.

### 10. Sulphur in Its Relation to the Other Members of Its Periodic Group.

Sulphur is found in the sixth group of the Periodic Classification. Associated with it are found oxygen, selenium (Se), and tellurium (Te). Each of the members of this group form hydrogen compounds—hydrides—of the general formula $H_2E$, such as $H_2O$, $H_2S$, $H_2Se$, and $H_2Te$. The oxygen compound, $H_2O$, as we know, is an odorless liquid at ordinary temperatures, while the others are nauseating, poisonous gases.

Sulphur, selenium, and tellurium each combines with oxygen forming similar oxides—$SO_3$, $SeO_3$, and $TeO_3$ and $SO_2$, $SeO_2$, and $TeO_2$. The members of this family or group pass by regular gradation from the gaseous, non-metal, oxygen to the almost metallic, slightly basic tellurium. Of the four elements, their abundance in nature is inversely proportional to their atomic weights: tellurium exists only in very small quantities, while oxygen is found in abundance.

### 11. The Properties of Ammonia.

Ammonia ($NH_3$) is a gas which is obtained as one of the products when animal or vegetable remains are heated without access of air, as is done when coal is heated in gas manufacture. Am-

monia is also made by the direct union of its constituent elements, nitrogen and hydrogen. Ammonia is a colorless gas with a strong suffocating odor. It is about one-half as heavy as air. It can be liquefied by pressure, and its boiling point is —33.5° C. It is very soluble in water: under a pressure of 1 atmosphere. 1 volume of water at 0° C. dissolves 1298 volumes of ammonia, and 1 volume of water at 20° C. dissolves 710 volumes of the gas.

When dissolved in water, a part of the ammonia is hydrated to $NH_4OH$. This substance ionizes into $NH_4^+$ and $OH^-$ ions. On account of the similarity between the $NH_4^+$ ion and the sodium or potassium ions, the $NH_4^+$ ion is called *ammonium*. (Note the termination *ium!*)

The hydration of ammonia is a reversible reaction and leads to equilibrium relations expressed schematically as:

$$NH_3(\text{gas}) \rightleftarrows NH_3(\text{dissolved})$$

$$NH_3(\text{dissolved}) + H_2O \rightleftarrows NH_4OH$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

Hence there are *three* distinct equilibria in any aqueous solution of ammonia; a removal or increase in any member of any of the equilibria will cause a shifting of the entire equilibria chain in such a direction as to adapt itself to the change. (Le Chatelier's principle.)

**Experiment.**—(a) Heat a small piece of gelatine in a dry test-tube. Note the odor (?).

**Experiment.**—(b) Secure a small flask (200-300 c.c. capacity), a one-hole stopper, and a piece of ordinary narrow glass tubing about eight inches in length. Push the glass tube barely through the hole in the stopper, and put the latter in the neck of the flask so that the tube will extend outward. Secure an ordinary, narrow-mouth bottle (not thin walled!) of any capacity from one-fourth to a whole liter, fit it with a one-hole stopper and short piece of glass tubing, one end of which has been drawn out to a fine opening, and which has been thrust through the cork so that the fine opening points *into* the bottle.

Pour about 25 c.c. of concentrated aqueous ammonia (sp. gr. 0.90) into the flask, insert the stopper with the glass tube, place the flask on an iron ring-stand in position to be heated, and clamp or suspend the bottle, mouth open and inverted, in such a position that the glass tube from the flask extends well into the bottle.

Warm the liquid gently with a small flame. When it is noticed that ammonia is escaping freely into the room, the bottle is probably full of the gas. In the meanwhile, secure a pan full of tap-water, and add 6 to 10 drops of phenolphthalein to it. Then, while keeping the bottle constantly in a vertical position, raise it until it is "clear" of the glass tube, put the stopper with the glass nozzle into the mouth of the bottle, and lower it, mouth downward, into the pan of water. What property of ammonia gas does the result show?

**Experiment.**—(c) Secure two burettes, fill one with dilute hydrochloric acid and the other with dilute ammonia solution. Measure into a

small, clean dish, 10 c.c. of ammonia solution, add one or two drops of methyl-orange to it (this is a "neutrality" indicator), and from the other burette, add dilute hydrochloric acid drop by drop while agitating or stirring the mixture with a clean glass rod so that every drop added may be mixed immediately with the rest of the liquid in the dish. When the indicator changes its color from yellow to pink, all of the ammonia has been neutralized.

Evaporate the liquid by putting the dish on top of a beaker which is just a little narrower than the dish. Fill the beaker half full of tap-water, put a piece of wood or paper between the dish and the beaker to provide an opening for the steam to escape, and heat the beaker. When evaporation on this "water-bath" is complete, note the appearance of the solid in the dish, taste it, and finally place the dry dish with its content on a clay-triangle, and the latter on a ring of an iron ring-stand so that the dish will be in position to be heated. Heat it fairly strongly, and note that the white solid—the ammonium chloride—is readily volatilized. In this respect it differs radically from sodium chloride, which cannot be volatilized except slightly at "white" heat. This difference in the properties makes it possible to remove ammonium chloride from its mixtures with this or other salts such as the chloride of potassium, magnesium, calcium, strontium and barium.

The "white cloud" observed when ammonium chloride is volatilized consists of fine particles of the salt in the solid form which are formed as soon as the gas is cooled.

Ammonium chloride is also formed by direct union of ammonia gas ($NH_3$) with hydrochloric acid gas (HCl), according to the equation—

$$NH_3+HCl=NH_4Cl.$$

Since these two gases are formed extensively, by vaporization, from their concentrated solutions, this formation of $NH_4Cl$ from its gaseous components is readily shown by putting a few drops of *concentrated* ammonia solution into a beaker, dipping a glass rod into some concentrated hydrochloric acid, and lowering the dipped end of the rod into the beaker. Try it.

Ammonium salts exhibit appreciable dissociation into $NH_3$ and the constituent acid which, as in all such dissociations, increases with rise of temperature. Ammonium bicarbonate dissociates even at ordinary temperatures so that it gives out an odor of ammonia. Slight warming increases the odor very much. When ammonium chloride is heated, the odor of ammonia is not observed because HCl also is volatile, and the cool mixture which strikes the nose contains only $NH_4Cl$. But if we use an ammonium salt composed of a non-volatile acid (e. g., ammonium sulphate or phosphate), then we may become aware of the dissociation which takes place on heating because the $NH_3$ gas alone will be vaporized.

**Experiment.**—(d) Put a little ammonium carbonate into a small dish, note its odor, then warm it and note the odor again. Try some ammonium sulphate in the same way. Write the equation for the dissociations of these two substances, respectively, including therein the additional dissociation of $H_2CO_3$ into $H_2O$ and $CO_2$, but leaving $H_2SO_4$ intact.

### 12. Nitrogen in Its Relation to the Members of Its Periodic Group.

Nitrogen appears as the type element of Group V in the Periodic Classification. Associated and closely related with it are the elements phosphorus, arsenic, antimony, and bismuth, the atomic weights of these gradually rising from N=14 to Bi=208. Again, in this family or group of elements, we have a gradual transition from the non-metallic (the lighter elements) to the metals (the heavier elements). Nitrogen and phosphorus are typical non-metals or acid formers, while antimony and bismuth are quite metallic in nature or base formers. The intermediate arsenic possesses both non-metallic and metallic properties; hence it is frequently called a *metalloid*.

Four of the elements of this group form similarly constituted compounds with hydrogen: $NH_3$ (ammonia), $PH_3$ (phosphine), $AsH_3$ (arsine), and $SbH_3$ (stibine); the most stable of these is ammonia and the least stable is stibine. The stability of these hydrogen compounds decreases with the increasing atomic weight of the group elements. The bismuth hydride is too unstable to form under workable conditions.

All the elements of this group unite with the halogens (chlorine, for example), forming compounds having the following formulæ:

$$NCl_3,\ PCl_3,\ AsCl_3,\ SbCl_3,\ \text{and}\ BiCl_3.$$

These compounds also exhibit a gradation of properties, especially in stability: nitrogen trichloride is an extremely unstable liquid which decomposes with explosive violence under the least provocation, while bismuth trichloride is a very stable solid.

The elements of this group also form similar oxides, a typical series being

$$N_2O_5,\ P_2O_5,\ As_2O_5,\ Sb_2O_5,\ \text{and}\ Bi_2O_5.$$

The study of the oxygen compounds of nitrogen will be reserved for a later chapter, for the considerations underlying this study are too complex to be understood by the student now.

### 13. The Fundamental Relation Which Brings About the Metathetical Reactions Between Ammonium Salts and Strong Bases.

**Experiment.**—Put some dry ammonium chloride into each of two test-tubes; do the same with ammonium sulphate: add to one portion of ammonium chloride and to one portion of ammonium sulphate a little sodium hydroxide solution, and to the other portions some slacked lime and a few drops of water. Warm the mixtures and note the evolution of ammonia. These mixtures first react metathetically to form $NH_4OH$, and then this substance dehydrates. Write the equations.

### 14. Exercise.

1. Point out the fundamental relation which brings about a metathetical reaction between any ammonium salt and any strong base.

2. What equilibria are present in an aqueous solution of ammonia?

3. Write in proper order the equations for the reactions that take place when ammonia gas is absorbed in dilute sulphuric acid.

### 15. The Properties of the Halogens, the Elements of Group VII.

The four elements, fluorine, chlorine, bromine, and iodine, are the members of Group VII of the Periodic Classification, and as a family of elements they have properties which are either the same in all of them, or they differ gradually in the order which they appear in the group according to the gradual increase of atomic weight (from Fluorine=19 to Iodine=127). The halogens derive their name from the fact that their sodium salts so closely resembles sea salt (which is principally NaCl)—the term *halogen* meaning *sea salt producers.*

The first two members are gases, the third a liquid, and the last a solid; in appearance they pass gradually from a light yellow to a purplish-black. The table below presents these facts:

| Element | Boiling Point | Physical State | Color | Atomic Weight |
|---|---|---|---|---|
| Fluorine | —187° C. | light gas | pale yellow | 19.0 |
| Chlorine | — 34° | heavy gas | greenish-yellow | 35.5 |
| Bromine | + 59° | liquid | red | 79.9 |
| Iodine | +184° | solid | purplish-black | 126.9 |

The halogens are extremely active elements, but they exhibit a gradual decrease of chemical activity with increasing atomic weight. Thus, in the case of their direct union with hydrogen, when fluorine and hydrogen are brought in contact, the union takes place with explosive violence even *in the dark.* Chlorine and hydrogen, however, do not unite in the dark, but they unite explosively in bright light or sunlight. Bromine vapor and hydrogen do not unite even in sunlight, but require the application of a flame, while iodine vapor and hydrogen require strong heating and a catalyst (spongy platinum) to effect a combination. The following thermo-chemical equations express strikingly this gradation:

$H_2+F_2=H_2F_2+77{,}000$ cals.

$H_2+Cl_2=2HCl+44{,}000$ cals.

$H_2+Br_2=2HBr+16{,}880$ cals.

$H_2+I_2=2HI-12{,}080$ cals.

All four of these hydrogen halides are colorless gases with pungent, irritating odors. When condensed at low temperatures or under great pressure in the absence of water they form liquids with the following boiling points:

| Compound | Boiling point (760 mm.). |
|---|---|
| $H_2F_2$ | +19.5° C. |
| HCl | —83.1° C. |
| HBr | —73.0° C. |
| HI | —34.1° C. |

It will be noticed that the above boiling point series is not regular, the irregular compound being $H_2F_2$. This compound does not have the simple formula as the three others, but is double the others; i. e., is *polymerized*. It is a general fact that the first member of a group of elements always shows quite a deviation in properties from those of the rest of the group. Thus, the compounds of fluorine often show distinct differences in behavior; like the irregularity in the gradation of the group boiling points of the hydrogen compounds. Another irregularity of fluorine can be shown in the fact that aqueous solutions of the hydrogen compounds of all the halogens, except fluorine, are good conductors of the electric current: $H_2F_2$ is a relatively poor conductor. This aberration of the first element of a group has already been pointed out in the case of the sixth group, where oxygen in its behavior often differs markedly from sulphur, selenium, and tellurium in many cases. Oxygen alone of this group forms a halogen compound of the type $ClE_2$—i. e., $ClO_2$, chlorine dioxide. Then, too, its hydrogen compound is a liquid at room temperature, while those of the others are gases.

The hydrogen compounds of the halogens are all very soluble in water: 506 volumes of HCl gas will dissolve in *one* volume of water at 0° C. and 760 mm. of pressure.

Other physical and chemical properties of the halogens and the halogen halides will be pointed out in the following articles and experiments; attention will also be called again to the exhibition of the gradation of properties in the mutual replacing power of the halogens. (See Art. 19.)

### 16. The Preparation of Chlorine.

The reactions involved in the preparation of chlorine involve entirely different fundamental facts than the metathetical reactions studied at present, hence the preparation of chlorine really does not fit in here. However, it is desirable to demonstrate here the properties of the element, and hence its preparation must be given. The details of the reactions involved in the preparation of chlorine need really not be considered here and the general fact alone need be learned that oxidizing agents react with hydrochloric acid to give water and free chlorine. The oxidizing agents may be considered to be suppliers of oxygen merely, and the oxygen they supply reacts with the hydrochloric acid according to the following equation:

$$O+2HCl=H_2O+Cl_2.$$

The portion of its oxygen which an oxidizing agent may be able to give up to be used according to the foregoing equation depends upon the kind of products that the other components of the oxidizing agent form simultaneously in such a reacting mixture, and since we are here not directly interested in learning the latter facts, it is really superfluous to consider these reactions any further. But since many texts give these extra details, and since it will not be amiss to satisfy a student's possible desire for an illustration, we will give the details of these reactions with two of the simplest illustrations.

When potassium chlorate is mixed with concentrated hydrochloric acid, all of the oxygen of the chlorate is used up according to the reaction above, and the remaining constituents (KCl) remain as a compound by themselves. Hence we have—

$$KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2.$$

When manganese dioxide is mixed with concentrated hydrochloric acid, one-half of its oxygen is used in accordance with the reaction—

$$O(\text{from } MnO_2) + 2HCl = H_2O + Cl_2$$

while the remainder (MnO) acts as a base, giving—

$$MnO + 2HCl = MnCl_2 + H_2O.$$

The sum of these two reactions gives the whole reaction—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The substances used in the following test-tube trial all act as oxidizing agents with concentrated hydrochloric acid—i. e., they give up a fraction of their oxygen to be used according to the equation—

$$O(\text{from Ox. agent}) + 2HCl = H_2O + Cl_2.$$

**Experiment.**—(a) Put into separate test-tubes a pinch of each of the following substances: manganese dioxide, lead dioxide, potassium chlorate, potassium nitrate, potassium permanganate. Add a few drops of concentrated hydrochloric acid upon each one of these powders and hold the test-tubes up to the light to see the greenish yellow gas generated by the mixture. Do not inhale the gas! It is likely to produce nausea and inflammation of the lining of the throat.

Another way to prepare chlorine is to treat bleaching powder—chloride of lime, $CaOCl_2$—with an acid. Bleaching powder is made by exposing lime to chlorine gas: the two combine to form a compound with the formula given above. When an acid is added to this substance, reaction takes place in such a manner that the lime appears to be neutralized by the acid, and the chlorine is set free. Since chlorine is a powerful germicide and bleaching agent, bleaching powder is used frequently in daily life, and the reaction just described is of great practical importance.

In the following experiment, the acid used is hydrochloric acid and the mixture reacts according to the following equation:

$$CaOCl_2+2HCl=CaCl_2+H_2O+Cl_2.$$

**Experiment.**—(b) (If possible, this whole experiment should be done out doors.) Secure the apparatus used for the preparation of carbon dioxide, put a handful of bleaching powder into the flask, moisten it with a little distilled water, and *when ready to collect* the chlorine gas, allow concentrated hydrochloric acid to drip slowly upon the bleaching powder. Secure four wide-mouth bottles of 300-500 c.c. capacity, four pieces of glass for covers and a piece of stiff paper or cardboard—about 3x3 inches:—perforate the latter in the center, slip the conducting tube from the chlorine generator through the perforation, and use the card as a cover while filling the bottles. Fill the bottles with chlorine and set them aside each covered with a piece of glass.

Dip a little cotton into hot turpentine and thrust the cotton into a bottle full of chlorine. Result? Into another bottle sprinkle a little powdered antimony. Result? Expose some moist colored calico to chlorine gas for ten to fifteen minutes. Result?

Secure a hydrogen generator, attach a glass nozzle to its delivery tube, turn on and light the hydrogen gas (small flame!) and project the flame into the last bottle full of chlorine. Test for the presence of the compound formed by this combustion by putting some ammonia solution on a piece of filter paper and holding it in the mouth of the bottle.

To get rid of the chlorine still in the bottles, they may be left, uncovered, out doors; or they may be filled with tap-water (out doors!) or, a little concentrated ammonia may be added to each bottle, the bottle closed with a piece of glass, and shaken vigorously. Ammonia reacts with chlorine according to the equation—

$$2NH_3+3Cl_2=N_2+6HCl.$$

The bottles should then be washed, and turned upside down to drain.

### 17. The Preparation of Hydrochloric Acid Gas.

**Experiment.**—(a) Prepare some hydrochloric acid gas by adding concentrated sulphuric acid to test-tubes containing sodium chloride, ammonium chloride, and magnesium chloride, respectively. Try also the effect of concentrated phosphoric acid and of concentrated acetic acid, respectively, on sodium chloride. The formation of hydrochloric acid gas may be revealed by holding a glass rod with a few drops of aqueous ammonia on it near the mouths of these test-tubes.

The reactions between these chlorides and acids are all metathetical reactions, but all the acids act with one $H^+$ in the molecule. Thus, for sodium chloride and sulphuric acid, the equation is—

$$NaCl+H(HSO_4)=NaHSO_4+HCl.$$

This is due to the fact that all the mixtures contain an excess of acid, and hence only *acid-salts* are formed.

On account of the great solubility of HCl in water, dilute acids cannot be used to prepare gaseous HCl.

Since we know that the reaction in the above mixtures is a

*metathetical* reaction, the following relation must be true of these mixtures:

$$[H^+]\times[Cl^-] > [H^+]\times[Cl^-]$$

In mixture before reaction takes place — In resulting mixture

This shows why water must be kept out of the mixture. If water were present, there would be many $H^+$ and $Cl^-$ ions retained by the mixture. It is evident that in the absence of water the mixture (i. e., the concentrated acid) does not retain these ions.

**Experiment.**—(b) Secure the flask and fittings used for the preparation of carbon dioxide; put a handful of common salt into the flask, add a little water to make a thick mush with the salt, and when ready to collect the gas, allow concentrated sulphuric acid to drip upon the salt. Collect an ordinary, narrow-mouth bottle (not thin walled) full of the gas, and ascertain its solution by thrusting the mouth of the bottle into a basin full of water.

Note the general resemblance in the kinds of materials used for the preparation of $CO_2$ (or $H_2CO_3$), $SO_2$ (or $H_2SO_3$), and HCl: in each case a *salt* of the *desired* acid is treated with another acid.

### 18. The Preparation of Hydrobromic and Hydriodic Acid Gases by Metathetical Reaction and the Liberation of the Non-Metals from Them.

**Experiment.**—(a) Put some potassium bromide crystals into a test-tube, cover them with concentrated phosphoric acid, and warm the mixture: to reveal the hydrobromic acid gas formed, dip a glass rod into ammonia and bring it near the mouth of the test-tube. What are the fumes formed? Then try, in the same way, potassium iodide with concentrated phosphoric acid (and with glacial acetic acid!). Set the test-tubes on your test-tube rack.

From the above trials, and from the experiments of Arts. 1 and 21, it is seen that a general method for the preparation of the hydrogen—halides from the metal—halides is given by the statement: treat a metal-halide with a concentrated, non-oxidizing and non-volatile acid. To illustrate why the choice must be limited to a *non-oxidizing* acid, the following experiment is given:

**Experiment.**—(b) Cover some potassium iodide crystals with concentrated sulphuric acid, and warm the mixture. What is the coloration due to?

**Experiment.**—(c) Take the test-tubes (set aside in (a)) and add a pinch of manganese dioxide to the contents of each, and warm the mixture. What is obtained now? What would have been obtained with chlorides? What general statement could be made regarding the obtaining of the free element of the non-metals from halide compounds?

### 19. A Demonstration of the Mutual Replacing Power of the Halogens.

**Experiment.**—To a solution of potassium bromide, add some chloroform and some chlorine water; the latter will form bromine by reaction. Shake the mixture; the chloroform collects the bromine because the latter is more soluble in chloroform than in water. Repeat the whole, using potassium iodide in place of potassium bromide. Finally treat some potassium iodide solution with bromine water and chloroform.

In these reactions the free element present at first displaces the combined element. This power of displacement is in the order: chlorine, bromine, iodine. This should be remembered. The equations for the reactions are very simple; e. g., $2KBr+Cl_2=2KCl+Br_2$. Write the others.

The foregoing experiments are intended to show that in many respects the halogens are entirely alike in properties, and that their differences in properties exhibit a *gradation*. The most important property in which they show a gradation is their tendency to change from the free element to the form of simple (binary!) compounds with metals or hydrogen: this tendency is greatest in fluorine and least in iodine, with the others in between in the order: fluorine, chlorine, bromine, iodine.

### 20. The Properties of Fluorine and of Hydrofluoric Acid.

Fluorine and hydrogen fluoride are, in some respects, markedly different from other halogens and other halogen hydrides respectively; hence the most important differences, or the peculiarities of fluorine,—are to be pointed out here.

When $Cl_2$, $Br_2$ and $I_2$ dissolve in water they remain unchanged except small amounts which react according to the equation—

$$X_2+HOH=HX+HOX.$$

but fluorine reacts with water immediately and completely when it comes in contact with it, according to the equation—

$$2F_2+2H_2O=2H_2F_2+O_2.$$

It is on this account that no demonstrations are made here with the *element* fluorine.

Hydrofluoric acid is notably different from the other halogen hydrides in the fact that its solution in water is a weak acid, while the solutions of HCl, HBr and HI are strong acids; and by the more striking fact that it reacts with sand, $SiO_2$ (or with glass, which is a fused mass rich in sand or a compound of sand), according to the following equation:

$$SiO_2+2H_2F_2=SiF_4+2H_2O.$$

This reaction takes place with both gaseous $H_2F_2$ or with an aqueous solution of $H_2F_2$. In the absence of water, silicon tetra-

fluoride escapes because it is a gas, while in the presence of water it remains in the solution.

**21. The Preparation of Hydrofluoric Acid, and the Action of the Latter on Glass.**

**Experiment.**—Mix a little calcium fluoride and concentrated sulphuric acid in a test-tube. Warm the mixture and allow the gas evolved to act on the sides of the test-tube for fifteen minutes or more. Wash out the test-tube, allow it to dry, and then examine it (?). Note the similarity between the preparation of this gas and that of hydrochloric acid gas, and hence make your conclusions as to the conditions that bring about the metathetical reaction between calcium fluoride and concentrated sulphuric acid.

**22. Practically Important Chemical Properties of Silica and of Silicates.**

Pure sand ($SiO_2$) does not react with any acid except hydrofluoric acid; it is not acted upon by any other solutions except solutions of strong bases—NaOH and KOH. The action of the latter results in the formation of silicates—$Na_2SiO_3$ or $K_2SiO_3$, which are soluble in water. The action takes place very slowly with NaOH solution, but with solid caustic soda which has been melted by heating it to a high temperature, the reaction takes place in a few minutes, according to the equation—

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O.$$

This reaction shows that silica ($SiO_2$) resembles carbon dioxide in its chemical properties. Note the relative positions of carbon and silicon in the table of the Periodic System of Elements.

Sodium silicate is also formed when sand is "fused" with solid sodium carbonate. The following equation expresses the reaction:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

In practice, a mixture of equal parts of sodium carbonate and of potassium carbonate is employed, because this mixture has a lower melting point than either ingredient alone.

**Experiment.**—*The fusion of sand or silicates with alkali carbonates, and the preparation of gelatinous silicic acid.*

Secure about 20 grams of sodium-potassium carbonate and 4 grams of sand, grind the sand to an impalpable powder in a mortar, then add the $NaKCO_3$, and grind the two together until they are intimately mixed.

Secure a medium-sized crucible, cover this with its lid, and place it on a clay-covered triangle,—and the latter, in turn, on the ring of an iron ring-stand—in position to be heated with a blast-lamp. Secure some metal tongs to handle the lid when it is hot.

Put about one-fifth of the sand and carbonate mixture into the crucible, cover the latter, and heat it with a moderate blast-flame until the mixture in it has fused to a clear liquid. Then add another portion, use it, and so continue until all of the substance has been melted. Then allow the crucible and contents to cool, put it into a medium-sized beaker, add distilled water until the crucible is submerged, and heat the water gently until the fused mass has been thoroughly disintegrated, and the crucible is practically free from it. Filter the liquid. The solid residue

present is undecomposed sand, in the main. The clear solution contains the alkali silicate and the excess of alkali carbonate. To the filtrate add small portions of concentrated hydrochloric acid, until, after stirring, the mixture contains an excess of acid. Test with litmus! Note the formation of a white, flocculent precipitate in appearance similar to $Al(OH)_3$: this is hydrated silica or silicic acid, $H_2SiO_3$ or $H_4SiO_4$. Evaporate the mixture on a water bath, and note that just before the mass became dry, it has the appearance of a gelatinous material similar to "cooked sago." This is silicic acid. Leave the dish on the water bath until the residue is dry:—a white impalpable powder remains—this is $SiO_2$, silica.

### 23. Compounds of Silica—Silicates.

A large part of the earth's crust is made up of compounds of silica. Many different kinds of rocks, potter's clay, and a large part of the alluvial soil is composed of silicates. Among the manufactured articles composed of silicates, we have brick, tile, pottery, porcelain ware, and glass. All silicates are insoluble except those of the alkalies. The latter, e. g., $Na_2SiO_3$, mixed with water, form transparent masses, which are soluble in water, and are known as *water glass.*

### 24. The Melting Points of Silicates—The Most Important Fact About Them.

The fusion of silicates occurs in the fluxing of ores, in glazing pottery, in vitrifying bricks, and above all in the manufacture of glass. In all of this work, the general fact is made use of that mixtures of silicates of two or more metals have lower fusing points than their components have separately.—and the fusion point of a mixture varies with the proportions of the ingredients: with the aid of tables of fusion points of mixtures, the chemical engineer has the material put into a furnace in such proportions that the mass may fuse at the lowest temperature.

### 25. The Analysis of Silicates.

Most of the insoluble silicates are like sand in their behavior with solutions of acids or of alkali hydroxides. In order to ascertain the bases in them, they must be fused with $NaKCO_3$ just as the sand was fused above, the fused mass treated with HCl and evaporated by dryness. The residue thus obtained from a *silicate* contains chlorides of the bases together with $SiO_2$. This residue is treated with dilute HCl and water to dissolve the salts of the bases present, the mixture is filtered to remove the $SiO_2$, and the filtrate is used to find the bases by the regular procedure. (Shown in a later chapter.)

### Questions on Chapter VIII.

1. What is the commercial source of ammonia? What is the commercial source of sulphur? What are the *allotropic* forms of carbon?

2. (a) What chemical changes take place when carbon dioxide dissolves in water? (b) What further action takes place if this water also holds a base in solution (e. g., sodium hydroxide)—the base being present in relatively large amount? (c) After enough of the carbon dioxide has been passed into the solution to change all the sodium hydroxide to normal sodium carbonate, if then the stream of carbon dioxide is continued, what further change will take place?

3. (a) Give the equations for all the reactions if the base in (2) were lime. (b) State what would be *observed* if the resulting solutions were boiled? Give the equations for this last change. (c) Point out where these reactions take place in nature.

4. (a) Show by formulæ what is meant by "step dissociation" of carbonic acid. (b) When a so-called insoluble carbonate, such as marble, is acted upon by an acid, the number of carbonate ions per c.c. furnished by the dissolution of the marble is naturally very small. Since the metathetical reaction takes place as with sodium carbonate, there must be a particular combination of ions which tends to remain so nearly completely combined that even the small number of carbonate ions from the dissolved marble will be *made less* by forming this combination; what is this combination?

5. How much carbon dioxide could be obtained by means of 5 grams of hydrochloric acid?

6. Describe how sulphur dioxide was prepared in the laboratory; give the chemical equation for the reaction of the substances in this preparation and the properties of this substance which have been shown you experimentally.

7. Write in proper order the equations for the reactions that take place when sulphur dioxide is absorbed in an excess of sodium hydroxide. If the addition of sulphur dioxide is continued beyond the point of neutralization of the sodium hydroxide, what new reaction will set in? Give the equation for the latter.

8. Mention the elements known as the halogens. In what respects are they alike? What is the order of their atomic weights? of their physical appearance, and of their tendency to form simple compounds with hydrogen or with metals? How was the latter demonstrated to you experimentally?

9. How was chlorine prepared from hydrochloric acid? Tell what you know concerning this reaction. State briefly the properties of chlorine that you have become acquainted with in the laboratory. How does hydrofluoric acid act upon glass or sand? Give the equation of this reaction.

## CHAPTER IX.

## THE RELATIVE WEIGHTS OF MOLECULES.

### 1. Introduction.

The fact that all gases, irrespecture of their chemical nature, undergo the same change in volume with the same change of pressure (law of Boyle) or with the same change of temperature (law of Charles) led scientists, long ago, to the conclusion that gases have the simple structure and behavior outlined in Chapter IV. According to this view, all the molecules of any particular gas are composed of a fixed number of atoms. A study of the condensation of gases to liquids has resulted in the conclusion that the molecules of the latter forms are practically identical with the molecules of the gases from which they are condensed. Hence the determination of the number of atoms in the molecules of different gases or gasified substances gives us a knowledge of the molecular weights of practically all forms of matter.

### 2. History of Determination of Molecular Weights.

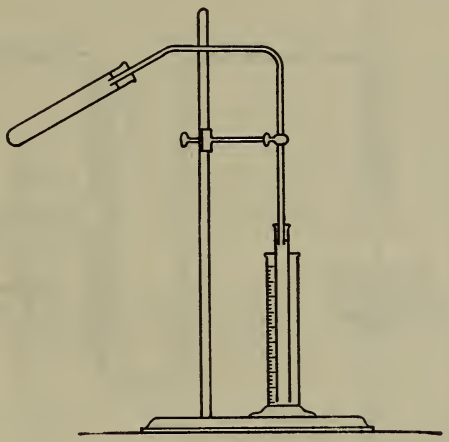
Our ability to determine the amount of matter in the molecule of any particular substance began with the wonderful prediction of Avogadro,—which production has since been established as a fact—that equal volumes of all gases, at the same temperature and under the same pressure, contain the same number of molecules. This knowledge enables scientists to ascertain the *relations* between the molecular weights of different gases as may be seen from the following illustration: A liter of hydrogen at 0° C. and 760 mm. weighs 0.08987 grams and a liter of oxygen under the same conditions weighs 1.429 grams or sixteen times as much. Since equal volumes of all gases under the same conditions contain the same number of molecules—which number we denote by *n* (we need not know its real value!)—then one molecule of hydrogen weighs $0.08987 \div n$ and one molecule of oxygen weighs $1.429 \div n$, and each one of the latter is $(1.429 \div n) \div (.08987 \div n)$ or again 16 times as heavy as a molecule of hydrogen. Or, in other words, the molecular weights are in the same ratio as the weights of equal volumes of the gases (at the same temperature and pressure!)

But the foregoing does not give us the *absolute* value of a single molecule: it merely enables us to get other values after we have one absolute value to begin with; and before we can employ the foregoing we must secure the molecular weight of at least one substance *by some other means*. We will now show how the latter was accomplished.

Early in the nineteenth century, Gay-Lussac, a French scientist, observed that, at the same temperature and pressure, two volumes of hydrogen unite with just one volume of oxygen, no more, no less; that one volume of chlorine gas units with just an equal volume of hydrogen, etc.; in other words, he observed that gases which reacted chemically do so in *simple volume ratios.* The following experiments are intended to acquaint the student direct with this simplicity of these volume relations:

**Experiment.**—(a) *To Demonstrate the Ratio by Volume Between Oxygen and the Sulphur Dioxide Formed From It.*

The apparatus to be used in this experiment is shown in the accompanying figure. Some heavy petroleum or lubricating oil is poured into the measuring cylinder; the test tube is detached and filled with oxygen (by displacement of air) and a little piece of roll sulphur is dropped into it. It is then attached again. Some of the oil is now drawn out of the cylinder so that, when the enclosed gas expands later on the oil will not flow over the top of the cylinder. Note where the level of the



oil is within the tube, then heat the sulphur cautiously: when the sulphur burns, the enclosed gases will expand, but on cooling they will contract until the level of the oil is again at the place at which it was before the sulphur was burned. This shows that sulphur dioxide occupies the same volume as the oxygen from which it is formed.

**Experiment.**—(b) *To Demonstrate the Ratio by Volume in Which Oxygen and Nitric Oxide React.*

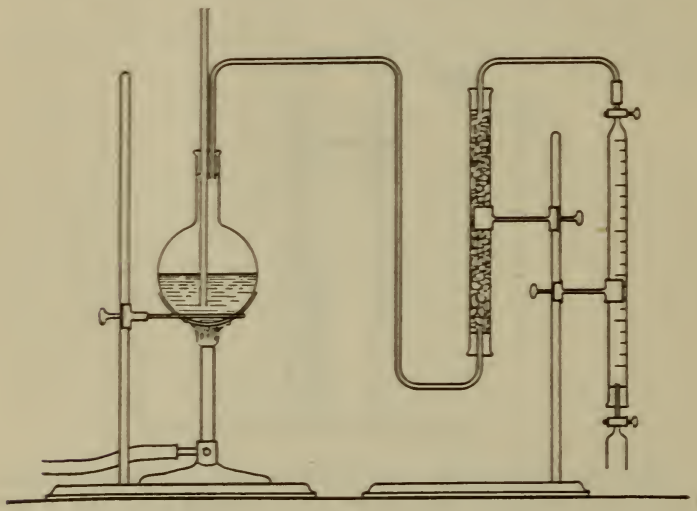
The instructor will furnish the oxygen and the nitric oxide for this experiment.

Each student should fill, over water in a large pan, a test-tube nearly full (not quite full) with nitric oxide gas, and another test-tube nearly full of oxygen gas. Mark, with rubber bands, the position of the surface of the water in both test-tubes. Then transfer a small amount of the nitric oxide to the oxygen test-tube, by tilting the former with its mouth under the latter. Nitric peroxide will be formed immediately, but will dissolve in the water gradually. The whole of the nitric oxide

should be transferred gradually to the oxygen test-tube. When the colored gas has been absorbed by the water, and the level of the latter does not rise any more, mark this final position of the water with another rubber band. Empty the tubes, and, by means of water drawn from a burette, measure the volume of the nitric oxide used, and of the oxygen used (not the volume of the remaining oxygen!). The ratio by volume in which nitric oxide reacts with oxygen will thus be found to be 2:1.

**Experiment.**—(c) *To Demonstrate the Ratio by Volume Between Ammonia Gas and the Nitrogen Obtained From It.*

The apparatus to be used is shown in the accompanying figure, except that the conducting tube should lead from the flask to the top of the drying tube or tower *instead* of leading to the bottom of the drying tube—as shown in the figure. The drying tube or "tower" should be at least 50 cm. in length, and 3 to 4 cm. in diameter. It should be filled with lumps of absolutely fresh quicklime. Instead of the burette shown in the figure, a glass tube 1 cm. in diameter and 60-80 cm. in length may be employed. The rubber stoppers, dropping funnel, and stop-cocks used for the ends must *fit absolutely air-tight*. Special attention must be given to this



point. Concentrated aqueous ammonia is put into the flask, and a small flame is applied to it. When enough ammonia has passed through the apparatus and burette to have swept out all the air, then the stop-cocks at the ends of the burette tube are closed. 50 to 100 c.c. of a "warm" concentrated solution of chloride of lime is then prepared and poured cautiously through the funnel into the burette, care being taken not to let air enter or gas leave the burette.

When no more of the liquid is drawn into the tube the stop-cock is closed and the burette is laid aside until it has cooled down to the temperature of the room. Then the lower stop-cock is opened *while this end is under water;* thus the pressure within the burette is made practically the same as the atmospheric pressure. It is then seen that the nitrogen in the tube occupies just one-half the volume occupied by the

ammonia from which it was formed. The chlorine in the chloride of lime combined with the hydrogen of the ammonia and left the nitrogen free.

The next step in the development of this subject was the recognition that this simplicity of the volume relations between the amounts of gases used up or formed by chemical reaction,—that these simple relations establish simple relations between the numbers of atoms in the molecules of the gases involved in the same reaction. Thus, the result of the first experiment above shows that there are as many *atoms of oxygen* in the *molecule of sulphur dioxide* as there are in each *molecule* of oxygen. (Why? Employ Avogadro's law in your consideration.) Again, the result of the second experiment shows that there must be at least two atoms in the molecule of oxygen because since two volumes of nitric oxide combine with 1 volume of oxygen, 2 molecules of nitric oxide use up 1 molecule of oxygen, and each molecule of nitric oxide receives the contents of one-half a molecule of oxygen: hence, the oxygen molecule must be divisible into two equal parts—i. e., it must contain 2 atoms or a multiple thereof.

The third experiment shows with its volume relations that the total number of ammonia molecules in the tube form one-half as many nitrogen molecules, and since one atom is the least amount of nitrogen that each molecule of ammonia can contain, it follows that each molecule of nitrogen has received at least 2 atoms.

The same argument applied to similar experiments has shown that hydrogen, oxygen, and chlorine, also, have at least two atoms in their molecules.

But there is no reason why this number of atoms in the molecules of these gaseous elements should be greater than two: hence for simplicity's sake we shall consider it to be a settled fact that the number of atoms in a molecule of these gaseous elements is *only* two.

The latter definite conclusion gives us the desired molecular weight of at least one substance—hydrogen—because with two atoms in the molecule, and with the atomic weight of hydrogen known to be 1—(because we made it the *unit* of *atomic* weights), *two* must be the molecular weight of hydrogen.

### 3. The Procedure for Obtaining Molecular Weights.

The preceding paragraph gives us the following general rule for the determination of the molecular weight of a substance: ascertain the weight of any definite volume of the substance in gaseous form at any temperature and pressure that may be convenient or necessary, reduce this by calculation to the weight of 1 liter, at 0° C. and 760 mm., divide this result by the weight of 1 liter of hydrogen under the same (standard) conditions (what significance has this resulting number?) and multiply the result by 2 (or more

accurately by 2.016, because the atomic weight of hydrogen is really 1.008).

*Problem:* 330 cc. of steam, at 130° C. and under 700 mm. pressure, weigh 0.1255 grams. Calculate the molecular weight of steam.

#### 4. The Gram-Molecular Volume of Gases.

The calculation of molecular weights has been made more simple by the following procedure: ascertain the volume of hydrogen which will contain as many grams of hydrogen as the number expressed by its molecular weight—that is, divide 2.016 by 0.089s7: this gives 22.4+ liters. Since any other gas will contain the same number of molecules in this volume under the same conditions, we have the following general result: the weight in grams of 22.4 liters of any gas at 0° C. and 760 mm. is the number which expresses its molecular weight. Hence 22.4 liters is called the gram-molecular-volume.

#### 5. Remarks on the Molecular Weights of Various Substances.

As mentioned before, most gaseous elements have two atoms in each volume; e. g., $H_2$, $O_2$, $N_2$, $Cl_2$, etc. But the elements of the "zero" group of the Periodic System (which see) have only one atom in each molecule. This may be connected with the fact that these elements—helium, neon, argon, krypton, xenon, niton—form no compounds, and hence their atoms appear to be utterly devoid of any combining tendency.

At high temperatures (1500° C. and above), the vapors of tin, sodium, potassium, silver and iodine are monatomic: this is due, undoubtedly, to the dissociating effect of the high temperature, mentioned in Chapter IV, Art. 6. At temperatures but slightly above its boiling point (184° C.), iodine is diatomic ($I_2$), while arsenic and phosphorus at corresponding temperatures are tetratomic ($As_4$, $P_4$), and sulphur has the formula $S_6$. The latter decreases as the vapor is heated to higher temperatures.

In contradistinction to elements, most gaseous *compounds* have the simplest molecular composition possible; e. g., water, $H_2O$, carbon dioxide, $CO_2$; hydrochloric acid, HCl, etc.

#### 6. For Gases, the Chemical Equation, Written with Correct Molecular Formulae, Expresses Their Volume Relations.

When the formulae of gases give their molecular composition, then the chemical equations express not only weight relations but also the relations between the volume of the gaseous substances in the equation. The coefficients of the molecules of gaseous substances give the volume of relations direct; e. g.:

$2H_2 + O_2 = 2H_2O$
2 vol. : 1 vol. : 2 vol. (steam)

$S + O_2 = SO_2$
1 vol. : 1 vol. (See Exp. (a) above.)

$C + O_2 = CO_2$
1 vol. : 1 vol.

$2C + O_2 = 2CO$
1 vol. : 2 vol.

$2NO + O_2 = 2NO_2$
2 vol. 1 vol. (See Exp. (b) above.)

$3Cl_2 + 2NH_3 = N_2 + 6HCl$
In solution 2 vol. : 1 vol. In solution. (See Exp. (c) above).

## CHAPTER X.

## THE ACTIONS AND USES OF GENERAL REAGENTS FOR SOLUTIONS OF SALTS.

### 1. Introduction.

There are some substances which react with salts for many metals and which are employed to produce desired combinations of ions or to establish the presence or absence of various metal ions in solution: such substances are called *general reagents.* Since the reactions which most of the common reagents undergo with salts of the common metals are *metathetical* reactions, they can be understood fully by the student in this period of his progress in chemistry, and the action and use of these reagents may be studied here with profit.

Although a general knowledge of the solubilities and degrees of ionization of these reagents and of the various compounds of the metals enables one to foresee many of the reactions that could take place between them, yet there are some reactions which cannot be foreseen because they involve a more accurate knowledge of solubilities and degrees of ionization or of still other special facts. Some of this more accurate knowledge of solubilities, of degrees of ionization, and of other special facts forms an essential part of chemical information, and is therefore given in this chapter.

In the selection of the facts, experiments and exercises of this chapter, the salts of the following metals are considered: $Ag^+$,

| | |
|---|---|
| $Hg^+$, $Hg^{++}$, $Cd^{++}$, $Pb^{++}$ | $Zn^{++}$, $Mn^{++}$, $Ca^{++}$, $Sr^{++}$, |
| $Cu^{++}$, $Bi^{+++}$, $Al^{+++}$, | $Ba^{++}$, $Mg^{++}$, $K^+$, $Na^+$, $NH_4^+$. |
| $Fe^{+++}$, $Fe^{++}$, $Ni^{++}$, | |

#### SODIUM (OR POTASSIUM) HYDROXIDE AS A REAGENT.

The following statement of *General Facts* and Table of Results of Action of Sodium Hydroxide should be read over once; then the operations in the exercise should be carried out very carefully and completely with *one* of the salt solutions; then with another salt solution, etc. Two objects are to be attained through the experimental operations: neat and correct manner of handling apparatus, and a definite knowledge of the appearance and behavior of the precipitates, etc. The latter should be committed to memory.

### 2. General Facts.

By strict *metathetical* reaction, the mixing of sodium hydroxide with solutions of salts of all metals except those of which the hy-

droxides are soluble should give a precipitate of the metal hydroxide—e. g., $CdCl_2+2NaOH=Cd(OH)_2+2NaCl$. However, in many cases the substances finally obtained are not the hydroxides of the metals but substances derived from them through one or both of the two following additional changes:

(a) Dehydration,—complete: $Hg(OH)_2$ to $HgO$; or partial: $Cu(OH)_2$ to $Cu_3O_2(OH)_2$.

(b) Dissolution of the precipitated hydroxide by excess of the reagent, which shows that the precipitated hydroxide functionates as an acid; e. g., $Zn(OH)_2$ dissolves in excess of NaOH solution as per equation:

$$H_2ZnO_2+NaOH=Na_2ZnO_2+2H_2O.$$

The formula for zinc hydroxide is thus written to *suggest its functionating as an acid.*

### 3. Results of the Action of Sodium (or Potassium) Hydroxide Upon Aqueous Solutions of Salts of the Common Metals.

$Ba^{++}$—Ppt. $Ba(OH)_2$: Is precipitated only from concentrated solutions because it is soluble one part in 20 parts of water; when precipitated: white.

$Sr^{++}$—Ppt. $Sr(OH)_2$—white: Soluble 1 part in 60 parts of water; not precipitated from dilute solutions.

$Ca^{++}$—Ppt. $Ca(OH)_2$—white: Soluble 1 part in 700 parts of water; not precipitated from *very dilute* solutions.

$Mg^{++}$—Ppt. $Mg(OH)_2$—white: Soluble 1 part in 6000 parts of water.

$Al^{+++}$—Ppt. $Al(OH)_3$—white and gelatinous: Soluble in excess of reagent, forming $NaAlO_2$, an aluminate.

$Zn^{++}$—Ppt. $Zn(OH)_2$—white: Soluble in excess of reagent, forming $Na_2ZnO_2$; a zincate.

$Pb^{++}$—Ppt. $Pb(OH)_2$—white: Soluble in excess of reagent, forming $Na_2PbO_2$; a plumbite.

$Fe^{++}$—Ppt. $Fe(OH)_2$—white when pure: Darkens on exposure to air (oxidizes partially to ferric state).

$Fe^{+++}$—Ppt. $Fe(OH)_3$—reddish brown and flocculent.

$Mn^{++}$—Ppt. $Mn(OH)_2$—"flesh" colored: Darkens on exposure to the air (oxidizes partially to manganic state).

$Ni^{++}$—Ppt. $Ni(OH)_2$—pale green.

$Cu^{++}$—Ppt. $Cu(OH)_2$—bluish white: Soluble in large excess of reagent; in hot solution it is dehydrated, forming CuO, a black ppt.

$Cd^{++}$—Ppt. $Cd(OH)_2$—white.

$Bi^{+++}$—Ppt. $Bi(OH)_3$—white.

$Ag^{+}$—Ppt. $Ag_2O$—grayish brown.

$Hg^{+}$—Ppt. $Hg_2O$—black: mercurous oxide.

$Hg^{++}$—Ppt. $HgO$—yellow: mercuric oxide; in order to avoid the formation of differently colored basic salts, the mercuric salt must be poured into the reagent.

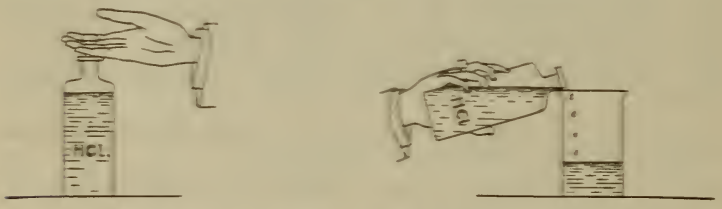
**4. Experiment on the Use of NaOH as Reagent.**

Secure solutions of water soluble salts of the following cations: $Cu^{++}$, $Ag^{+}$, $Zn^{++}$, $Cd^{++}$, $Hg^{+}$, $Hg^{++}$, $Pb^{++}$, $Fe^{++}$, $Fe^{+++}$, $Ni^{++}$, $Al^{+++}$, $Mg^{++}$, and $Ca^{++}$.

To a few cubic centimeters of each of these solutions in a test-tube, add a few drops of sodium hydroxide solution, shake each mixture and note its appearance; then add a few drops more of the reagent, and so continue until the reagent has been added in a relatively large amount, say, about twice as much reagent by volume as of salt solution, if the two solutions are of approximately equivalent concentrations. Compare the results with the statements in the table above.

Place the test-tube and contents on the test-tube stand, and make a note book entry of the work just done. Put down a heading stating the salt worked with, and under this describe the appearance of the precipitate. State how it behaves with excess of the reagent and give all equations of changes which take place.

The next operation has for its object the reversal of the change produced by the sodium hydroxide. For this purpose, the precipitate or the solution is to be treated with a dilute acid (hydrochloric or nitric acid) according to (a) or (b) below.




Method of Handling Reagent Bottles

(a) If the metal hydroxide did not dissolve in excess of sodium hydroxide, then, before adding the acid decant the supernatant liquid as completely as possible without disturbing the precipitate. To this residue, or to the solution produced by excess of the sodium hydroxide, add a small amount of an acid (the accompanying sketch shows how reagent bottles should be handled). Stir the mixture, add another small amount of the acid and stir, and thus continue until the precipitate is dissolved by means of the least amount of acid. Write the equation of this reaction.

(b) *If the metal hydroxide dissolved in excess of sodium hydroxide*, drop into the solution a piece of litmus paper, add a few drops of an acid, stir the mixture, add more of the acid, and so continue until the litmus paper indicates that the solution is practically neutral:—practically all of the metal hydroxide will then have been precipitated again. Allow the precipitate to settle, decant the supernatant liquid, and dissolve the precipitate with as *slight* an excess of hydrochloric (or nitric) acid as possible.

The action of the acid upon this solution requires some explanation. The dissolving of a metal hydroxide in excess of sodium hydroxide is a *reversible* reaction, which is *forced to completion* by the presence of more sodium hydroxide than is used up in the reaction: when an acid is added to such a solution the excess of sodium hydroxide is done away with (equation?) and the reversible reaction in question then takes place simply in the reverse direction from that in which it just took place, and the precipitate reappears. Thus when an acid is added to a solution of $Na_2ZnO_2$, the following reaction takes place gradually as the excess of NaOH is diminished:

$$Na_2ZnO_2 + 2H_2O \rightleftarrows 2NaOH + Zn(OH)_2.$$

NOTE.—The student should try to remember the color and general appearance of each solution and precipitate handled.

**5. Illustrations of Various Uses of Sodium Hydroxide as a Reagent.**

(a) To remove a metal ion completely from a solution: When enough sodium hydroxide has been added to a solution of a "ferric" salt to change all of the $Fe^{+++}$ ion to $Fe(OH)_3$, and the precipitate has been allowed to settle, then the addition of a drop more (which is generally spoken of as *an excess*) will not produce a change, and the fact that all of the $Fe^{+++}$ ion has been precipitated is indicated by the fact that the upper, clear part of the solution will remain clear on the addition of this extra drop of sodium hydroxide solution. Would all this apply as well to a solution of an aluminium salt? Hence, for which metals only may sodium hydroxide be used as a precipitate? See table above.

(b) As a *separating* agent. This will be illustrated with the following experiment:

**Experiment.**—*The Separation of Copper from Zinc* (from brass). Dissolve small amounts of brass pieces by placing them in a small evaporating dish, and adding the *least amount* of a mixture of concentrated nitric acid plus an equal volume of water which will dissolve them. Put the dish on an improvised water bath, and evaporate the contents to dryness. Add a few c.c. of distilled water to dissolve the salts in the dish. Then place about 15 c.c. of sodium hydroxide and about 45 c.c. distilled water into a beaker and heat the contents to boiling. Into this boiling solution add the solution from the dish, a little at a time with constant stirring, until all has been added. Enough sodium hydroxide should be present to have precipitated all the copper as copper oxide and to have dissolved the zinc as sodium zincate. Allow the copper oxide to settle, and decant the liquid into another beaker. Add water to wash the copper oxide free from the adhering solution; then decant and discard this wash water. Wash the copper oxide a second time in the same manner; then dissolve it in the least amount of dilute sulphuric acid, and evaporate the solution to such an extent that copper sulphate crystals will separate from it on cooling.

Into the solution in the other beaker drop a piece of litmus paper, add a few drops of hydrochloric acid, stir the mixture, add a few drops more and so continue until the litmus indicates that the solution is neutral. Most of the zinc hydroxide will then have been precipitated. Decant as much of the liquid as possible, then pour it upon as large a filter paper as you have. See the accompanying sketch for method of folding filter paper, and for correct manner of pouring liquids on filter papers. Use a wooden funnel stand: the *rust* from iron stands is liable to drop into the filtrate. When most of the liquid has been removed by filtration, transfer the contents of the filter to a small dish, add concentrated hy-

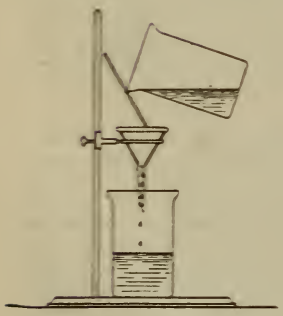
Filter.

Folded once.

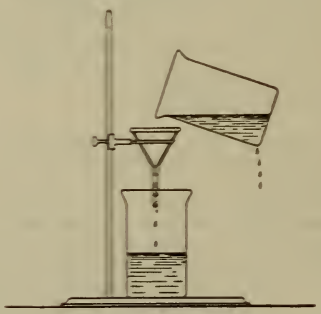
Folded twice.

Opened.

Directions for folding filter paper.



Correct Filtering.



Incorrect Filtering.

drochloric acid, a few drops at a time, until the zinc hydroxide has dissolved. Then evaporate the solution until everything that is volatile has been expelled. A molten residue of zinc chloride will remain. Select, from the table above, other pairs of metals which may be separated in this way by means of sodium hydroxide.

The following experiments make use of the same facts and prin-

ciples as the foregoing, but they employ the cheapest soluble hydroxide that occurs in commerce, and they illustrate two very important industrial operations. They are also intended to teach the student correct chemical manipulation.

### 6. The Old Commercial Preparation of Sodium (or Potassium) Hydroxide.

Weigh out roughly 25 grams of anhydrous sodium carbonate or 67 grams of crystalline Sal Soda ($Na_2CO_3 \cdot 10H_2O$), place it into a large porcelain dish, add about 250 c.c. distilled water, and heat the solution until it boils. In the meanwhile calculate how much slaked lime would react with this amount of sodium carbonate; then calculate how much quicklime would be necessary for this much slaked lime; then weigh out roughly one and one-half times as much quicklime as calculated, place it into a small dish, add distilled water to slake it (warming the dish, if necessary, to start the action), and then add enough water to make the lime into a thin paste. Pour this paste gradually, with stirring, into the boiling soda solution. (Care should be taken to have the volume of the boiling soda solution about 250 c.c.). What reaction takes place? Continue boiling for a few minutes—Why? Pour the mixture into the smallest beaker that will hold it, and allow it to settle.

In the meanwhile secure two burettes, and fill one with normal sulphuric acid (N $H_2SO_4$). Fill the second burette with some of the clear part of the sodium hydroxide just prepared. Measure out accurately 10 c.c. of this into a beaker, dilute with water, add a drop of an "indicator of the point of neutrality" (methyl orange) and titrate with the normal sulphuric acid. Note the number of c.c. of the normal sulphuric acid used. By means of a measuring cylinder, measure the volume of the sodium hydroxide solution (without the main part of the sediment). Be sure to drain the liquid well from the sediment—the total volume of the sodium hydroxide solution should include the amount in the burette plus the 10 c.c. used for titration.

In order to ascertain the amount in grams of sodium hydroxide obtained, answer the following questions and make the calculations indicated:

(a) How many grams of sulphuric acid does 1 c.c. of a normal sulphuric acid solution contain?

(b) How many grams of sodium hydroxide will this weight of sulphuric acid neutralize?

(c) The number of c.c. of normal sulphuric acid used for titration multiplied by the number of grams of sodium hydroxide neutralized by 1 c.c. gives the number of grams of sodium hydroxide in the 10 c.c. sample. Make this calculation.

(d) What *fraction* of the total volume of sodium hydroxide was the 10 c.c. sample? Multiply the result of (c) by $\frac{1}{X}$, where X= fraction of whole which 10 c.c. equals. This gives the *total* amount of sodium hydroxide produced.

(e) Compare this amount with the amount of sodium hy-

droxide which, according to calculation, should have been obtained from the amount of sodium carbonate taken at the beginning.

In your note book state what happens in each operation, and give equations.

**7. Normal Solutions: Their Significance and Methods of Preparation.**

*Definition:* A *normal* solution is such a solution which contains, *in one liter of solution,* the number of grams numerically equal to the molecular weight of the substance divided by the number of replaceable hydrogen atoms (or their metallic equivalent) in the molecule.

*Examples:* (a) A *normal* solution of hydrochloric acid contains 36.5 grams of acid per liter of solution ($HCl$: $(35.5+1)\div 1=36.5$).

(b) A *normal* solution of sulphuric acid contains 49 grams of acid per liter of solution ($H_2SO_4$: $(2+32+64)\div 2=49$). Sulphuric acid contains two replaceable hydrogens: hence the molecular weight is divided by *two*.

(c) A *normal* solution of potassium hydroxide contains 56.1 grams of potassium hydroxide per liter of solution ($KOH$: $(39.1+16+1)\div 1=56.1$).

(d) A 1/10 *normal* solution of barium hydroxide contains 8.568 grams of barium hydroxide per liter of solution ($Ba(OH)_2$: $(137.37+32+2)\div 2=85.68$). The metallic equivalent of barium is *two;* hence the molecular weight is divided by two.

(e) A *normal* solution of sodium chloride contains 58.5 grams of sodium chloride per liter of solution ($NaCl$: $(23+35.5)\div 1=58.5$).

(f) A *normal* solution of potassium sulphate contains 87.1 grams of potassium sulphate per liter of solution ($K_2SO_4$: $(78.2+32+64)\div 2=87.1$).

*Designation:* *Normal* solutions are mostly designated by the letter "N." and different concentrations are indicated correspondingly: e. g., tenth normal by N/10; twice normal by 2N. It may happen that the solution is not exactly the normality intended: e. g., it may only be 9/10 as strong as a normal solution. A "factor" is then applied: 0.9N, etc.

*Why Are Normal Solutions Used?* Suppose 0.5 grams of sulphuric acid is desired. It would be quite difficult to weigh out exactly 0.5 grams of sulphuric acid. But suppose a *normal* solution of sulphuric acid was available: One liter or 1000 c.c. contains 49 grams $H_2SO_4$, 1 c.c. contains 0.049 grams. Then

$$\frac{0.5}{0.049} = 10.2 \text{ c.c. would contain 0.5 gms. of } H_2SO_4.$$

Further, the statement can be made that 1 c.c. of a *normal* sulphuric acid solution is equivalent to 1 c.c. of a *normal* sodium hydroxide solution. Why is this true? The equation for the reaction is

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$
$$2(40) + 98$$

In words, $2\times40$ grams of sodium hydroxide react with 98 grams of sulphuric acid—or 40 grams with 49 grams of sulphuric acid. One liter of normal sodium hydroxide solution contains 40 grams per liter and *one* liter of sulphuric acid contains 49 grams of acid. Hence it is seen that 1000 c.c. of N NaOH neutralize 1000 c.c. of a N $H_2SO_4$ solution or 1 c.c. of N NaOH=1 c.c. of N. $H_2SO_4$.

HOW NORMAL SOLUTIONS ARE PREPARED FROM STOCK.

(a) *Normal Sulphuric Acid:* Required 49 grams of *pure* $H_2SO_4$ per liter of solution. Use C. P. sulphuric acid of sp. gr. 1.84, which is 96% pure. Use an accurate burette and measure out $\frac{49}{0.96\times1.84} = 27.74$ c.c. into a liter flask containing about 200 c.c. of distilled water and then add distilled water so that the solution, when cooled to 20° C., comes to the 1000 c.c. mark on the neck of the flask. This gives very nearly a normal sulphuric acid solution, which may be used (without further standardization) for all but the most accurate work.

(b) *Normal Potassium Hydroxide:* Required 56.1 grams of *pure* KOH per liter of solution. Use KOH sticks, "purified by alcohol," which contains about 88% of KOH. The amount required will be $\frac{56.1}{0.88} = 63.75$ gms. Weigh out this amount and place into a liter volumetric flask and add distilled water so that the total solution, when cooled to 20° C., is just 1 liter. This solution will in all probability *not* be exactly normal, since the purity of KOH sticks is *not* always 88%. The resulting solution should be titrated against a normal acid and a "factor" used.

(c) Normal *salt* solutions can be made by weighing out the required amount of salt (taking into account its purity and the water of crystallization) and adding distilled water to make up a liter of solution!

**8. The Commercial Purification of Crude Salt.**

Crude salt contains small amounts of calcium and magnesium chlorides and sulphates. The removal of these and of very small amounts of other

impurities is accomplished as follows in commerce:—weigh out roughly 100 grams of crude salt, dissolve it in 350 c.c. of cold water. Put the solution in a flask, and add about 10 c.c. of sodium hydroxide solution, heat the mixture to boiling and filter it through a large pleated filter (in a 4-inch funnel). Add another drop of sodium hydroxide to ascertain if enough of this has been used.—if not, add more and filter again. Then heat the mixture again to boiling, add about 5 c.c. of barium chloride solution to the hot mixture, allow the precipitate to settle out of the top layer and ascertain by means of an additional drop of $BaCl_2$ whether or not enough of this has been added—if necessary add more $BaCl_2$—and stir the mixture to distribute this new portion of reagent over the whole solution. Test again to find out if enough $BaCl_2$ has been added, and if necessary repeat this whole operation Then, without filtering, add about 20 c.c. of sodium carbonate solution. Ascertain, as before, that enough of this precipitant has been used, then filter through a fresh pleated filter. Heat the clear filtrate and add dilute hydrochloric acid, a few drops at a time, until after stirring and testing with litmus paper it is found that all of the excess of sodium carbonate has been neutralized.

Put the solution into a large clean dish, place this on a wire gauze, and heat it with two burners to concentrate the solution as rapidly as possible until it is in the form of a thin mush:—then pour it quickly on a large, smooth filter in a funnel.

NOTE.—Do not use metal tongs in handling hot beakers or dishes,—grasp them with the fingers on the extreme upper edge, place them quickly on a towel, and then handle them by the aid of the towel.

In the note book, state what each reagent does and give the reaction. Also state why the rapid evaporation and crystallization is necessary; and finally point out how the last *traces* of impurities in the solution are disposed of—or separated from the salt.

### 9. Ammonia as a Reagent.

*General Facts.*—Since a solution of ammonia contains $OH^-$ ion, its action on solutions of salt of the common metals might be expected to be similar to the action of sodium hydroxide. However, it differs from sodium hydroxide in several respects: it is a *weak base* (slightly ionized!), while sodium hydroxide is a strong base: and besides the ions and their combination, ammonia contains a great many $NH_3$ molecules, while sodium hydroxide contains nothing that corresponds to this $NH_3$. Hence it is not surprising that ammonia in its action as a reagent is, in general, different from sodium hydroxide.

The first, and most important, difference between sodium hydroxide and ammonia is the fact that ammonia, in the presence of its own salts, acts differently in many cases from the way it acts in their absence—while sodium hydroxide is not noticeably affected by the presence or absence of its own salts. Since an ammonium salt is always *produced* when ammonia acts as a reagent, we need only consider the effect upon other salt solution of *ammonia mixed with one of its own salts.*

**10. Effects Produced by the Addition of Ammonium Chloride and Ammonia to Solutions of Salts of Common Metals.**

$Na^+$, $K^+$, $Ca^{++}$, $Sr^{++}$, $Ba^{++}$:—no effect whatever because the hydroxides of these metals are strong bases.

$Ag^+$:—forms a ppt. of AgCl, which is dissolved by ammonia to form $Ag(NH_3)_2Cl$. This compound tends to dissociate into its original constituents—

$$Ag(NH_3)_2Cl \rightleftarrows AgCl + 2HN_3,$$

and it is stable only in the presence of free $NH_3$. Hence, when the excess of $NH_3$ in these solutions is neutralized by the addition of an acid to the mixture, the insoluble AgCl is obtained again.

$Pb^{++}$:—forms a ppt. of $PbCl_2$, and this is changed by ammonia to Pb(OH)Cl, an insoluble white compound.

$Hg^+$:—forms a ppt. of $Hg_2Cl_2$, and this is changed by ammonia to a *black,* insoluble mass, a mixture of mercury and of the compound $HgCl\ NH_2$, according to the equation:

$$Hg_2Cl_2 + 2NH_4OH = HgClNH_2 + NH_4Cl + Hg + 2H_2O.$$

$Hg^{++}$:—gives, on the addition of ammonia, $HgClNH_2$, a white compound insoluble in water. Treated with HCl, it forms $HgCl_2 + NH_4Cl$, which are soluble.

$Cu^{++}$, $Cd^{++}$, $Zn^{++}$, $Ni^{++}$:—they form soluble compounds of the general formula $M(NH_3)_4\ Cl_2$

$$\text{Or } M(NH_3)_4\ SO_4.$$

The *cations* of these salts are: $Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$, $Zn(NH_3)_4^{++}$, $Ni(NH_3)_4^{++}$. With colored salts—such as those of $Cu^{++}$ and $Ni^{++}$—the formation of the complex ions shows itself by a great deepening of the color.

The ammonia compounds tend to dissociate into their original constituents—

$$Cu(NH_3)_4SO_4 \rightleftarrows CuSO_4 + 4NH_3,$$

and they are stable only in the presence of free $NH_3$. Hence when the excess of $NH_3$ in these solutions is neutralized by the addition of an acid, the original simple salts (e. g., $CuSO_4$, in the illustration above) are obtained again.

$Fe^{++}$ and $Mn^{++}$:—these cations are not affected directly by $NH_4Cl + NH_4OH$, but in alkaline solutions they exert a great tendency to change to the trivalent form—$Fe^{+++}$ and $Mn^{+++}$—hence on contact with the air, these mixtures turn dark and gradually form precipitates of $Fe(OH)_3$ and $Mn(OH)_3$, respectively, because the change to the trivalent form is brought about by the oxygen of the air, according to the equation:—

$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3.$$

$Mg^{++}$:—not affected by $NH_4Cl + NH_4OH$.

$Bi^{+++}$, $Fe^{+++}$, $Al^{+++}$:—these ions are precipitated completely as hydroxides, $Bi(OH)_3$, $Fe(OH)_3$, $Al(OH)_3$.

**11. Rule for the Use of Ammonia as a Reagent.**

The foregoing may be summarized in the following *Rule for the Use of Ammonia as a Reagent:*

Always have a large quantity of an ammonium salt in a solution before adding ammonia. In such mixtures only salts of lead, of mercury, and of the trivalent metals give precipitates.

**12. An Explanation According to the Ion Theory of the Effect of Ammonium Chloride Upon Ammonia.**

The non-precipitation by $NH_4Cl—NH_4OH$ of $Mg^{++}$, $Fe^{++}$, and $Mn^{++}$ has not been accounted for in Art. 10 and is to be considered here.

To understand the effect of ammonium chloride upon ammonia, we must recall Question 7 in the "Questions on Chapter VII." It is shown in the solution to this question that an increase in the concentration of the $H^+$ ion (by the addition of HCl) brings about a decrease in the concentration of the other ion—the acetion.

A little consideration reveals that all the statements concerning acetic acid made in the solution to this question apply equally well to $NH_4OH$. When $NH_4Cl$ is added to a solution of ammonia, the number of $NH_4^+$ ions per c.c. is increased, and hence the number of $OH^-$ ions per c.c. will be decreased by the formation of unionized $NH_4OH$ molecules, just as in the illustration with acetic acid, an increase in $H^+$ ions brings about a decrease of acetions.

Since $NH_4Cl$ is largely ionized, while $NH_4OH$ is but slightly ionized, the $NH_4^+$ ions added by means of $NH_4Cl$ amount to an *enormous increase* in $NH_4^+$ ions in the solution, and hence bring about a correspondingly *large decrease* in $OH^-$ ions. This gives such a small concentration of $OH^-$ ions that such a solution would present—with the bivalent cations $Mg^{++}$, $Fe^{++}$, and $Mn^{++}$—the relation in the following illustration—

$$[Mg^{++}]\times[OH^-]^2 < [Mg^{++}]\times[OH^-]^2$$

Contents in mixture of $Mg^{++}$ salt. with $NH_4Cl$ and $NH_4OH$.

Contents in water saturated from solid $Mg(OH)_2$ in it.

Hence the combining tendency of the ions in the mixture on the left is too small to produce a ppt. of $Mg(OH)_2$. But with trivalent cations such as $Al^{+++}$, $Bi^{+++}$, $Fe^{+++}$, the reverse relations always holds—

$$[Al^{+++}]\times[OH^-]^3 > [Al^{+++}]\times[OH^-]^3$$

Contents in mixture of $Al^{+++}$ salt, $NH_4Cl$ and $NH_4OH$.

Contents in mixture saturated from solid $Al(OH)_3$ in it.

Hence the mixture on the left always reacts so as to produce $Al(OH)_3$.

To express, in a few words, this difference in the precipitation of these bivalent and trivalent metal hydroxides, we would say that the concentration of the $OH^-$ ion is too small for the precipitation of these bivalent, but large enough for the precipitation of all trivalent metal hydroxides.

NOTE.—With $Mg(OH)_2$, the concentration of the $OH^-$ ion has to be raised to the second power in expressing its effect upon the reacting tendency; with $Al(OH)_3$, the concentration of the $OH^-$ ion has to be raised to the third power: the concentration must always be raised to the power expressed by the number of parts taking part in the reaction—which is $2OH^-$ for $Mg(OH)_2$ and $3OH^-$ for $Al(OH)_3$. This relation is one of the fundamental facts in nature, and this whole relation between concentration and reacting tendency is known as the Law of Mass Action.

### 13. Illustration of the Action of Ammonia With and Without Ammonium Chloride with Solutions of Magnesium, of Ferrous, or of Manganous Salts.

**Experiment.**—Put into each of two test-tubes about 5 c.c. of a magnesium salt solution. To one test-tube, add a *few drops* of ammonia from the reagent bottle on the desk, and note that a precipitate is obtained. The reaction is metathetical:—write the equation.

To the other sample of magnesium salt, add an equal volume of ammonium chloride solution from the reagent bottle on the desk. Close the test-tube with the thumb (or with a suitable rubber stopper which should be kept on hand for the purpose) and mix the solutions by shaking the test-tube lengthwise vigorously. Then add a *few drops* of ammonia to the mixture: no precipitate should be formed. If any precipitate is obtained, then more ammonium chloride is required.

Repeat this trial with a sample of a manganous salt. The same results should be obtained with this salt.

### 14. Illustration of the Effects Produced by Ammonia on the Salts of the Common Metals.

**Experiment.**—To become familiar with the results produced when ammonium chloride and ammonia are added to solutions of salts of the common metals, secure twelve clean test-tubes, put them on the test-tube rack, and put into each one 2 c.c. of one of the solutions of the following salts:

$Ag^+$, $Hg^+$ $Hg^{++}$, $Cd^{++}$, $Pb^{++}$, $Fe^{+++}$, $Fe^{++}$,
$Cu^{++}$, $Bi^{+++}$, $Al^{+++}$, $Mn^{++}$, $Ca^{++}$,

Add to each one 2 c.c. of ammonium chloride solution. The solutions of $Ag^+$, $Pb^{++}$, and $Hg_2^{++}$ will give precipitates of the chlorides of these metals. A precipitate may also appear in the $Bi^{+++}$ solution: such a precipitate is BiOCl, a *basic* salt, formed on account of conditions which need not be considered here. To dissolve this precipitate add dilute hydrochloric acid, a few drops at a time, shake the mixture, and thus continue until the precipitate has been dissolved (changed to $BiCl_3$ by metathetical reaction:—$BiOCl+2HCl=H_2O+BiCl_3$).

None of the other mixtures will undergo any changes.

Next, add to each test-tube, in turn, a small amount (about 1 c.c. of

ammonia and shake the mixture:—if the ammonia produces a precipitate or appears to dissolve a precipitate that is present, add more ammonia, shake the mixture again, and so continue until the further addition of ammonia produces no further effect. Note the results and compare them with the foregoing list of results.

**15. Ammonia as a Means for Separating Cations.**

**Experiment.**—Secure about 10 c.c. of a solution containing bismuth and copper salts—or aluminium and nickel salts—or ferric and magnesium salts. Add to it ammonium chloride and ammonia in sufficient amount to precipitate the trivalent metal completely (how do you ascertain when *just enough* has been used?). Filter the mixture, transferring all the precipitate to the funnel. When all of the solution has drained off, fill the funnel full of distilled water; allow this to drain off completely, and again fill the funnel with water. Thus the precipitate is "washed" clean of any adhering portions of the original solution. When the funnel has drained clean again, put another clean receiver under the funnel, drip some dilute hydrochloric acid upon the precipitate until it is dissolved. What does the new solution contain? Give equations for all reactions. This exercise illustrates the use of ammonia as a *separating* reagent.

## HYDROGEN SULPHIDE AS A REAGENT.

NOTE.—Hydrogen sulphide is poisonous, hence generators of this gas should be used either outside of the building or in hoods in which there is a strong draft.

**16. Preliminary Consideration.**

Hydrogen sulphide is a weak acid: in its aqueous solution it is only slightly ionized into $2H^+$ and $S^{--}$. When the concentration of the $H^+$ ion in an aqueous solution of hydrogen sulphide is increased (e. g., by adding HCl), the concentration of the $S^{--}$ ion becomes less for the same reasons for which the concentration of the $OH^-$ ion in ammonia becomes less when the concentration of the $NH_4^+$ ion is increased.

**17. General Facts.**

The sulphides of the alkali metals and of the alkaline earth metals (Na, K, $NH_4$, Ca, Sr, Ba, Mg) are soluble in water; hence hydrogen sulphide does not react metathetically with solutions of salts of these metals. It does not react with salts of Al, because $Al_2S_3$ is decomposed by water, according to the equation—

$$Al_2S_3+6HOH=2Al(OH)_3+3H_2S.$$

All other sulphides are insoluble; hence hydrogen sulphide reacts metathetically with the neutral (or alkaline) solutions of salts of all metals except the above. With the twenty metal ions which we are considering in this chapter, the following precipitates would thus be obtained by metathetical reaction: $Ag_2S$, $Hg_2S$, HgS, CdS, PbS, CuS, $Bi_2S_3$, $Fe_2S_3$, FeS, NiS, ZnS, MnS.

But when a solution contains free $H^+$ ion in moderate concentration (when as much of a strong acid such as HCl, $H_2SO_4$ or $HNO_3$ has been added to it so as to give $[H^+]=0.2$ to 0.27 grams per liter) then hydrogen sulphide precipitates only the following sulphides (by metathetical reaction): $Ag_2S$, $Hg_2S$, HgS, PbS, CdS, CuS, and $Bi_2S_3$; and it does not precipitate the ions $Fe^{++}$, $Zn^{++}$, $Fe^{++}$ and $Mn^{++}$.

A solution of methyl violet may be used to determine the concentration of $H^+$ ion here required. Put two or three drops of such a solution in a clean porcelain dish, add a slightly larger number of drops of the solution to be tested and mix the solutions:—a blue tint shows that the solution to be tested has a lesser concentration of $H^+$ ion than is here required, a blue-green tint indicates the proper concentration of $H^+$ ion, and a yellow-green (or yellow) tint indicates *too great* a concentration of $H^+$ ion.

The following table presents the colors of methyl violet corresponding to certain approximate concentrations of $H^+$ ion, which is included for reference only:

| Conct. of $H^+$ | 1.000 N | 0.100 N | 0.010 N | 0.001 N |
|---|---|---|---|---|
| Color of methyl violet | yellow | green | blue | violet |

Since the core of most "indelible" pencils (violet) contain *methyl violet,* streaks of such a pencil, made on white paper, may be used in place of the methyl violet solution above: it is merely necessary to moisten these streaks with the solution to be tested.

Commit all the above general facts to memory.

**18. Explanation of the Difference Which $H_2S$ Shows in Its Effect When the $H^+$ Ion Concentration is Large or Small, Respectively.**

The above difference in the effect produced by $H_2S$ depends upon the following two fundamental facts (a) and (b). See also Article 12, which explains similar relations for ammonia.

(a) The concentration of the unionized $H_2S$ molecules is the same in all of its saturated solutions. Hence their ionizing tendency is the same in all solutions; and since the latter is equal to the combining tendency of the ions—that is, $k\times[H^+]^2\times[S^{--}]$, it follows that the value of the latter product is the same in all of these solutions saturated with $H_2S$. Hence, when $[H^+]$ has a large value (as in acidified solutions!) $[S^{--}]$ must have a small value, and when $[H^+]$ has a small value (as in neutral or alkaline solutions) $[S^{--}]$ has a larger value than in acidified solutions.

(b) The sulphides $Ag_2S$, $Hg_2S$, HgS, CuS, CdS, PbS, $Bi_2S_3$, which are precipitates *even* when the $H^+$ ion concentration is moderately large (as in acidified solutions), are less soluble than

those sulphides (ZnS, MnS, FeS, NiS) which are not precipitable out of acidified solutions.

Hence the former sulphides (CuS, etc.) have smaller amounts of unionized molecules in their saturated solutions (i. e., in mixtures from which they have been precipitated), and since the unionized molecules are in equilibrium with their ions, it follows also that the ion-products of the former sulphides (CuS, etc.) in mixtures from which they have been precipitated are smaller than the ion-products of the latter sulphides (ZnS, etc.) in mixtures from which these have been precipitated.

With these two facts—(a) and (b)—before us, it is evident that in the introduction of $H_2S$ into any solution containing simple salts of $Ag^+$, $Hg^+$, $Hg^{++}$, $Cu^{++}$, $Cd^{++}$, $Pb^{++}$, or $Bi^{+++}$, the products of the ions (e. g., $[Cu^{++}]\times[S^{--}]$) in the original mixtures will always—even in acidified solutions—be larger than the products of these ions in a solution saturated with the sulphide—(CuS), which is the *resulting* mixture. Hence, in the original mixture, the combining tendency of the ions is greater than their combining tendency *in the solution after reaction* when the combining tendency of the ions and the ionizing tendency of the unionized CuS are *in equilibrium*. Therefore the ions combine to form the precipitate of CuS. In symbols, this condition that brings about reaction is expressed thus:—

$$[Cu^{++}]\times[S^{--}] > [Cu^{++}]\times[S^{--}]$$

in original mixture before reaction. | in mixture after reaction—i. e., in a solution saturated with CuS.

But with salts of $Zn^{++}$, $Mn^{++}$, $Ni^{++}$, $Fe^{+++}$, and $Fe^{++}$, this relation exists only when $[S^{--}]$ is rather large, which is the case only in the *absence* of $H^+$ ions.

The following numerical values obtained from actual measurements presents these relations in a definite manner:

(a) Plain water saturated with $H_2S$ contains $(1/10)^{15}$ gram-ions of $S^{--}$ per liter.

(b) Acidified water (i. e., N/10 HCl) saturated with $H_2S$ contains $(1/10)^{21}$ $S^{--}$ per liter.

(c) Plain water saturated with zinc sulphide contains $(1/10)^{9.5}$ gram-ions of $Zn^{++}$, and also of $S^{--}$, hence the ion product for this solution is $(1/10)^{19}$.

(d) Plain water saturated with copper sulphide contains $(1/10)^{21}$ gram-ions of $Cu^{++}$, and also of $S^{--}$, hence the ion product for this solution is $(1/10)^{42}$.

(e) If a plain solution of an ordinary zinc salt containing (1/10) gram-ion of $Zn^{++}$ per liter were saturated with $H_2S$, and any possible precipitation were delayed temporarily, then the solu-

tion would contain enough $Zn^{++}$ and $S^{--}$ to give an ion product of $(1/10)\ (1/10)^{15}$ or $(1/10)^{16}$; and this would be greater than the ion-product of a saturated solution of zinc sulphide (see *c*); hence zinc sulphide would be precipitated from this solution.

Similarly, if a plain solution of an ordinary copper salt containing (1/10) gram-ion of $Cu^{++}$ were saturated with $H_2S$, and any possible precipitation were to be delayed temporarily, then the solution would contain enough $Cu^{++}$ and $S^{--}$ ions to give an ion-product of $(1/10)^{16}$; and this would be greater than the ion-product of a saturated solution of copper sulphide (see *d*); hence copper sulphide would be precipitated from this solution.

(f) But if, instead of plain solutions, acidified solutions of these zinc and copper salts, respectively, are employed, then the $S^{--}$ concentration produced by saturating them with $H_2S$ would be only $(1/10)^{21}$; and the product of the $Zn^{++}$ (or $Cu^{++}$) times the $S^{--}$ concentration would be $(1/10)^{22}$: for zinc, this last value is *smaller* than the ion-product of ZnS in a saturated solution of zinc sulphide, and hence no precipitation will take place; while, for copper, this last value still is larger than the ion-product of CuS in a saturated solution of copper sulphide, and hence precipitation will take place even with this acidified solution of copper salt.

Solutions of ordinary salts of $Ag^{+}$, $Hg^{+}$, $Hg^{++}$, $Cd^{++}$, $Pb^{++}$, and $Bi^{+++}$ behave like the $Cu^{++}$ solution above; while solutions of ordinary salts of $Mn^{++}$, $Fe^{++}$, $Fe^{+++}$, and $Ni^{++}$ behave like the $Zn^{++}$ solution above.

### 19. Colors of Precipitated Sulphides.

The colors of sulphides are a valuable means of identifying the metals. Freshly precipitated sulphides have the following colors:

FeS, NiS, $Ag_2S$, HgS, PbS, $Bi_2S_3$—dull black.
CuS—Brownish black.
ZnS—white (when pure!)
CdS—yellow.
MnS—pink or flesh color.

NOTE.—During precipitation, HgS frequently exhibits several other colors—black, yellow, red—but with excess of $H_2S$ it finally becomes black.

### 20. Reagents Which Act Upon Sulphides and Produce Soluble Compounds of Their Metals.

(a) Dilute HCl or dilute $H_2SO_4$ react *metathetically* with the following: ZnS, FeS, $Fe_2S_2$, MnS, CdS. (CdS requires a more concentrated "dilute" acid than the others.)

(b) $HNO_3$, dilute or concentrated, acts upon all the sulphides

under (a) and also upon the following: $Ag_2S$, PbS, CuS, $Bi_2S_3$, NiS. The reaction is complex and results in the formation of free sulphur and nitrates of the metals concerned.

(c) Aqua Regia—a mixture of concentrated hydrochloric acid and acid as oxidizing agent such as crystals of $KClO_3$ or concentrated $HNO_3$ (one-third of volume of HCl). This mixture acts upon all the sulphides under (a) and (b) and, in addition, upon HgS.

Aqua regia is essentially a concentrated solution of free chlorine, and this acts so as to produce free sulphur and the chloride of the metal concerned—e. g.—

$$HgS + Cl_2 = HgCl_2 + S.$$

**21. The Experimental Formation of the Insoluble Sulphides of the Common Metals.**

**Experiment.**—Secure 12 large test-tubes 16×150 mm. Put about 5 c.c. of a solution of each of the following metal ions into a test-tube and place them in the test-tube rack in the order in which they are here given:—$Ag^+$, $Hg^{++}$, $Hg_2^{++}$, $Pb^{++}$, $Cd^{++}$, $Cu^{++}$, $Bi^{+++}$, $Zn^{++}$, $Fe^{++}$, $Fe^{+++}$, $Ni^{++}$, $Mn^{++}$. To the last five add an equal volume of $NH_4Cl$ solution, and about 1 c.c. of ammonia (*vide*). Then add to every one about 15 to 20 c.c. of distilled water saturated with hydrogen sulphide. Shake the contents of each test-tube vigorously, then put the test-tube in the rack and allow the precipitate to settle.

Note the color of the precipitates (see Art. 21). Pour off the supernatant liquid as completely as possible without disturbing the precipitates. Then add to each test-tube a small amount of that particular reagent (given in the list in Art. 20) which will dissolve the sulphide considered, warm and shake the mixtures to hasten their action. The figure on page — shows how the test-tubes with liquids in them should be held when they are heated—the flame should be adjusted to a *medium small* size, and the heated end of the test-tube should be constantly shaken *across* the flame.

With the twelve mathematical equations for the precipitation of the twelve sulphides, but consider that, in the last five, the $H_2S$ first reacts with the ammonia (an acid with a base) to form ammonium sulphide, $(NH_4)_2S$, and then the latter substance reacts metathetically with the salts of $Zn^{++}$, $Fe^{++}$, $Mn^{++}$, $Ni^{++}$ and with $Fe(OH)_3$.

Next, *state* what has been formed from each precipitated sulphide when it was treated with the reagent selected according to Article 20, and write the equations for those reactions in which HCl and those in which aqua regia were used.

**22. A Demonstration of the Influence of the Hydrogen Ion Concentration Upon the Precipitation of Sulphides.**

**Experiment.**—Secure in a test-tube about 5 c.c. of a solution of a cadmium salt in water. Add to it an equal volume of ordinary dilute HCl—which contains about 3 gram-mols. of HCl per liter of volume (3 N HCl)—and test the effect of this mixture on methyl violet.—See last part of

Art. 17. The mixture contains about 1.5 gram-mols. HCl per liter, and with approximately 60% of this HCl in the form of ions, the mixture contains $1.5 \times .60 = 0.9$ grams $H^+$ ion per liter. This concentration of $H^+$ ion is too great to permit the precipitation of CdS even, as will be shown by the following trial:

Put the mixture into a flask (preferably an Erlenmeyer flask of about 300 c.c. capacity) which has been fitted with a one-hole rubber stopper (No. 5) and a short piece of narrow glass tubing which extends about half-way to the bottom of the flask and which terminates in a fine opening (nozzle). This end should not extend into the liquid (see foot note).

With the stopper resting *loosely* on top of the flask, let the $H_2S$ gas flow into the flask until most of the air in the flask has been displaced by $H_2S$. Then fit the stopper into the neck, and shake the flask vigorously to bring the liquid into intimate contact with the $H_2S$ gas and thus hasten the saturation of the liquid with this gas. If the acid used was not too dilute, no precipitate will appear in the liquid.

Next, add 50 to 60 c.c. of distilled water, and saturate the mixture again with $H_2S$ as before: a copious precipitate of CdS should have been formed. If not, add another 50 c.c. of water. Test, with methyl violet, the particular solution in which extensive precipitation takes place:—the indicator-mixture should give a blue-green color.

Now secure 5 c.c. of a zinc salt solution, add only 5 c.c. of dilute HCl, add 100 c.c. of water (twice as much as was used with cadmium), put the mixture in a 300 c.c. Erlenmeyer flask and saturate it with $H_2S$: no precipitate should appear. Add another 50 c.c. of water, and treat again with $H_2S$:—still no precipitate should be formed.

Next, add about 10 c.c. of ammonia solution from the reagent bottle on the desk. This solution contains about 4 gram-ions per liter and 5 c.c. of it is enough to neutralize the acid in the mixture. Saturate the mixture with $H_2S$ again and shake it:—a white precipitate of ZnS will be formed.

Read Article 17 again carefully, and note that this experiment demonstrates the facts therein presented.

### 23. An Illustration of the Use of Hydrogen Sulphide as a Reagent for Separating Certain Metal Ions.

**Experiment.**—Secure 10 c.c. of a solution of a mercuric salt and 10 c.c. of a solution of a nickel salt, add about 3 c.c. of dilute HCl, mix them in a 300 c.c. Erlenmeyer flask, test the mixture with methyl violet (see Art. 17), and add either water or dilute HCl as may be necessary to secure the $H^+$ ion concentration which will allow all of the mercuric ion to be precipitated, but which will prevent the nickel ion from being precipitated. Then treat the *cool* mixture with $H_2S$ gas as directed in the preceding experiment. Fit a filter paper carefully into a funnel, and hang the funnel on a wooden funnel stand in such a position that its stem will extend *into* a beaker placed underneath to receive the filtrate. The stem should touch the side of the beaker so that the filtrate will run down the side of the beaker instead of "splashing" down. Being *careful* in such

FOOT NOTE.—For convenience in class use, all students should be supplied with flasks which will fit the same sized stopper. The stopper and glass tube should be fastened in the hydrogen sulphide supply pipe. As long as the glass tube does not extend into the liquid, and terminates in a small opening, it will remain clean on the inside, and hence to clean it, as well as the stopper for the next time it is to be used, they need only to be wiped clean with a towel, or to be rinsed with a stream of water from a wash bottle.

manipulations is essential to success in this work! Filter the above mixture, using a stirring rod in pouring, as shown in the figure, Art. 5, which should be looked at carefully. Wash the precipitate twice with water as directed in Art. 15, and collect the wash-water with the filtrate.

A new precipitate may be formed when the wash water dilutes the filtrates,—but whether it does or not, test the acidity of the filtered liquid, dilute it if necessary, and treat it again with $H_2S$ to make certain that all of the mercuric ion has been precipitated: should more HgS be thus obtained, filter the solution through the same filter paper, and wash the latter again *twice*,—but throw these washings away.

*To dissolve the mercuric sulphide:* If the amount of precipitate on the filter is large enough, take it up with a small porcelain spoon and put it into a small clean porcelain dish. If there is not enough precipitate to handle it that way, open the filter paper, tear off all the paper parts which are not covered with precipitate, and put the paper with the precipitate on it into the dish. Cover the material in the dish with a small amount of ordinary dilute nitric acid, and warm the mixture. The precipitate may turn white or "cream" color, but a careful inspection will show that it is not dissolved. See Art. 20 to assure yourself that nitric acid should not attack HgS. Decant the liquid carefully, add a little water and decant again, throwing these liquids away as useless. Now put upon the material in the dish a small amount of concentrated HCl, *warm* the mixture, and add, gradually, several small crystals of potassium chlorate. When the precipitate has been acted upon, remove the floating lump of sulphur (and also the filter paper), and boil it for a minute or two to expel the chlorine. Then pour the solution into a labeled test-tube for *later use*. For an explanation of the reaction in this mixture see Art. 20 (c).

To the filtrate above from the precipitate of the HgS, add one-third its volume of $NH_4Cl$ solution, and then just enough ammonia so that, after thorough stirring, the mixture will emit the odor of free ammonia. This assures you that all of the free acid has been neutralized. Then add 10 c.c. of ammonium sulphide solution, stir the mixture, and filter it. To make certain that you have used enough $(NH_4)_2S$ to precipitate all of the $Ni^{++}$ ion, add a few drops more to the filtrate: if more precipitate is thus obtained, add several c.c. of $(NH_4)_2S$ to the filtrate and filter it through the same funnel. Again test as above to ascertain if precipitation is complete. When precipitation is complete, wash the precipitate on the filter twice with distilled water. Then put another receiver under the funnel and pour upon the precipitate on the filter some dilute HCl:—assure yourself from Art. 20 that this should produce no change. Wash off this acid with a little water, then transfer the precipitate to a dish as you transferred the HgS above, cover it with concentrated HCl, add a few drops of concentrated $HNO_3$, and warm the mixture: note from the color that a soluble Ni salt has been formed again (what is formed?) and then throw this material away.

Put into a separate test-tube a little of the mercuric chloride solution prepared above, and add to this an equal amount of stannous chloride solution:—a white precipitate ($Hg_2C_2$) or a grey precipitate (Hg) will be formed according to one of the following equations:

$$2HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2$$
$$HgCl_2 + SnCl_2 = SnCl_4 + Hg.$$

This behavior is characteristic of mercuric salts.

Put into your note book a *brief* account of all that has happened in this procedure, and give all equations.

**24. Exercise.**

The answers to the following questions are to be carefully arrived at, then written out, submitted to the instructor, and after they have been passed upon by him, they are to be carefully impressed upon your memory.

The following questions refer to the mixture worked in the preceding experiment:

1. If a magnesium salt is also present in this mixture, what becomes of the $Mg^{++}$ ion during the course of the procedure?
2. If silver salts are also present in the above mixture, what would happen at the beginning of the procedure? What would be the best method to remove the $Ag^{+}$ ion so that it would not interfere with the rest of the procedure as given?
3. If aluminium salts are also present in this mixture, what would happen to the $Al^{+++}$ ion in the course of the procedure?
4. What other metal ions, if present, would have shown the same behavior as the $Ag^{+}$ ion in Question 2 above?
5. What other metal ions, if present, would have shown the same behavior as the mercuric ion in the experiment above?
6. What other metal ions would have shown the same behavior as $Al^{+++}$ in Question 3 above?
7. What other metal ions would have shown the same behavior as magnesium in Question 1 above?

**25. The Formation of Free Sulphur From Hydrogen Sulphide by "Oxidizing Agents."**

Solutions of certain substances act upon $H_2S$ in such a manner as to change the $S^{--}$ ion to S°—i. e., sulphur—and when this takes place in dilute solutions, the sulphur remains finely divided and the liquid has a white, "milky" or turbid appearance.

**Experiment.**—(a) Put a few c.c. of a solution of ferric chloride into a test-tube, add a few drops of dilute HCl, and several c.c. of $H_2S$ water. Note the *appearance* of the liquid. Heat the solution to its boiling point for several minutes: most of the sulphur will collect into a few globules which will float on top of the liquid. The reaction in this mixture is expressed by the equation:—

$$2FeCl_3+H_2S=2FeCl_2+2HCl+S$$

The theoretical view of this change will be given in a later chapter.

(b) Put a few c.c. of ordinary dilute $HNO_3$ into a test-tube, heat the liquid, and add 2 to 3 c.c. of $H_2S$ water. Note the appearance of the liquid, and the presence of free sulphur in it. The following equation expresses the reaction in this mixture:—

$$3H_2S+2HNO_3=3S+4H_2O+2NO$$

This formation of free sulphur from $H_2S$ is frequently encountered, and the student should be familiar with the "white" appearance of the resulting solution. This change is also effected by the oxygen of the air,

$$H_2S+O=H_2O+S$$

and it is likely that the sulphur deposits in the earth which furnish us sulphur have been produced from $H_2S$, which originated far down in the earth and which was oxidized when it came in contact with air.

**26. The Separation of the Common Metals Into Five Groups for Qualitative Analysis.**

The experiment and the exercise just preceding show the student how these reagents may be used to separate metal ions (cations) and to recognize them by the formation or non-formation of certain compounds. The determination, by such means, of the *metal ions* and *acid ions* (anions) present in various salts, acids, and bases is called QUALITATIVE ANALYSIS. However, in the attempt to identify an unknown substance, use is made not only of the facts concerning the general reagents NaOH, $NH_4OH$, and $H_2S$, but also of the facts of solubility learned in Chapter VI and of special reactions peculiar to individual elements. With the aid of all the facts at our command, the search for and identification of the constituents of a salt, acid, or base would still be quite complex were it not for the organization of these facts. The general survey of the facts leads us to group the common metal ions into *five* main groups. This enables us, when working with an unknown mixture, to separate the metal ions into at least *five groupings,* if necessary; the task of identifying the constituents of each of the *five* groups becomes, then, a matter of less difficulty.

The *five* groups in our *qualitative analysis,* together with the metal ions which comprise each group, are:

1. *Insoluble Chloride Group.*
   $AgCl$, $Hg_2Cl_2$, $PbCl_2$.
2. *Acid Sulphide Group.*
   $HgS$, $PbS$, $Bi_2S_3$, $CuS$, $CdS$.
3. *Ammonium Sulphide Group.*
   $Al(OH)_3$, $Fe_2S_3$, $FeS$, $NiS$, $MnS$, $ZnS$.
4. *Alkaline Earth Group.*
   $BaCO_3$, $CaCO_3$, $SrCO_3$, $MgCO_3$.
5. *Alkali Group.*
   $Na^+$, $K^+$, $NH_4^+$.

Only tests for *simple anions* will be made in this course. The anions which will be tested for are $CO_3^{--}$, $Ac^-$, $Cl^-$, $SO_4^{--}$, $NO_3^-$, and $PO_4^{---}$. The directions for these tests are to be found in Art. 39.

The procedure which will be pursued in the work to follow is:

(1) To identify and confirm the members of the first group in solution singly as *knowns*. Anions are also to be determined.

(2) To separate, identify, and confirm the members of the first group in a mixture as *knowns*. Anions are also to be determined.

(3) To separate, identify, and confirm the members of the first group, singly or in mixtures, as *unknowns*. Anions are also to be determined.

(4) Each succeeding group will be tested just as the first group, solutions being used solely.

(5) After a complete survey of the field has been made by working with *known* and *unknown* acids, bases, and salts in solution, *unknowns* consisting of *solids* will be handed out for identification and separation. It is desired that the student should become familiar with the appearance and chemical behavior of special salts, oxides, and minerals. The student will be required to note in his note book all the facts of appearance and behavior peculiar to his particular unknown.

Mixtures may contain two or three different cations or anions, but care will be taken to avoid using or forming solids which are insoluble in acids or aqua regia (i. e., AgCl, $PbSO_4$, $BaSO_4$, $SrSO_4$, $CaSO_4$, and silicates). Phosphates of the third and fourth groups will be avoided and only those of the alkalies and of the first and second groups will be given out because the scheme below does not take care of others. Among these compounds will be included:—iron sulphide; iron pyrites or "fool's gold"; quicklime; manganese dioxide or pyrolusite; sodium phosphate; copper phosphate; red oxide of mercury; mercuric sulphide or cinnabar; lead sulphide or galena; zinc sulphide or sphalerite; ferric oxide or haematite; ferrous sulphate or copperas; ferrous ammonium sulphate or Mohr's salt; ammonia iron alum; potash alum; sodium carbonate or "washing" soda; sodium bicarbonate or "cooking" soda; magnesium sulphate or Epsom salts; sheet lead; commercial silver or Mexican silver coin; nickel coin; Monel metal (a nickel-copper alloy); and the *coatings* on galvanized iron or roofing tin.

### 27. Beginning of the Procedure for the Qualitative Analysis of Certain Compounds of the Common Metals with Some General Directions of Manipulation.

Make a heading in your note book designating and describing the substance which has been handed you to be analyzed.

The substance handed you may be in solid form (soluble in water or in acids) or in solution. The procedure to be followed is:

(1) *Solutions* are to be subjected at once to the regular procedure of the qualitative analysis scheme beginning with Art. 28. Only a portion (about one-third) of the sample given you should be used: reserve the remainder for "repeats" and the anion tests.

(2) *Non-Metallic Solids* should be powdered or crushed finely in a mortar. Put a "pinch" of it in a *clean* test-tube, add 5 c.c. of water, heat the mixture to boiling, and note if the solid is

soluble in water. If it is soluble in water, dissolve a larger portion (not all!) and proceed with the regular procedure as in (1).

If it is not soluble in water, decant all but 1 c.c. and add an equal volume of concentrated HCl. Heat the mixture and note if the solid dissolves. If the solid does not dissolve appreciably, try another pinch similarly in concentrated $HNO_3$. If it dissolves in neither one of these acids alone, add a little concentrated HCl to the test-tube containing the $HNO_3$. Shake and warm: the solid should dissolve in this mixture, because the student will not be handed a solid which will not dissolve in one of these media. A larger portion of the solid (not all!) should then be dissolved by whatever means it is necessary to employ. The greater portion of the acid employed then should be evaporated off (in a *clean* porcelain dish) and distilled water added. Proceed with the *clear* solution as in (1). Make a note book entry of all the reagents employed to dissolve the solid!

Substances *insoluble in water* may be oxides of metals, sulphides, carbonates, or phosphates. Concerning these substances, the student will recall (a) that all *oxides* of metals react with acids, (b) the various *sulphides* react with acids, as stated in Art 20, and (c) all *carbonates* and *phosphates* are dissolved by metathetical reaction with strong acids.

NOTE.—When an insoluble carbonate is acted upon by an acid and converted into soluble substances, the carbonic acid remains in solution but to a *very slight* extent only; but when an insoluble phosphate, such as $Ca_3(PO_4)_2$, is acted upon by a strong acid and changed to soluble substances, the acid or acid ion remains in solution. Thus, when calcium phosphate is dissolved by means of HCl, the following reaction takes place:

$$Ca_3(PO_4)_2 + 4HCl = 2CaCl_2 + Ca(H_2PO_4)_2$$

The primary calcium acid phosphate, $Ca(H_2PO_4)_2$, ionizes extensively into $Ca^{++}$ and $2(H_2PO_4)^-$ ions, but not materially into $2H^+$ and $PO_4^{---}$ ions. Hence the solution contains $Ca^{++}$ ions, $H^+$ ions (from HCl), $Cl^-$ ions, and $(H_2PO_4)^-$ ions, with a certain proportion of all the possible combinations as unionized portions. When a base (e. g., ammonia) is added to such a mixture, the *acid* salt is converted to a *normal* salt: the soluble primary calcium acid phosphate is converted into the insoluble normal calcium phosphate:—

$$Ca(H_2PO_4)_2 + 2CaCl_2 + 2NH_4OH = Ca_3(PO_4)_2 + 2NH_4Cl + 2H_2O$$

(3) *Metallic Substances* should be cut into small particles, placed in a beaker or dish, covered with a little distilled water, and an equal volume of conc. $HNO_3$ added. Warm this mixture: if the whole does not gradually and completely dissolve, add more of the acid in small amounts. When all of the metal has dis-

solved, evaporate most of the acid by gentle heating (on an asbestos board high above the flame). If an insoluble powder has been formed by the action of the acid, *decant* the liquid from it or remove by filtration, and proceed with *part* of the clear liquid as in (1).

State in your note book whether or not the metal changed entirely to *soluble* compounds.

An insoluble powder formed during the entire acid treatment is either antimony or tin oxide, but these are not to be considered in this analytical work, and hence such residues may be thrown away.

**28. Determination of the Cations—Group I: Metals Whose Chlorides Are Insoluble.**

A solution of any compounds soluble in *water or nitric acid* may contain $Ag^+$, $Hg^+$, $Pb^{++}$,—hence when enough of a chloride is added to such a solution, these cations will be *completely* precipitated (except the slight amount of $Pb^{++}$ which corresponds to the perceptible solubility of $PbCl_2$).

*Preliminary Trial to Ascertain if Any of These Metals Are Present.*—Put 1 c.c. of a solution that *could contain* (*?*) *these* cations in a test-tube, add ten drops of dilute HCl and shake the mixture. A permanent (see *Note* below) precipitate shows that one or more of the cations of this group are present, and they should be precipitated out of a large amount of sample as directed below. In the absence of a precipitate, nothing further in this article nor in Art. 29 applies to this solution, and the next trials with it are to be made according to Art. 30. In any case, the mixture made in this preliminary trial will not be needed further.

NOTE.—If the solution contains salts of bismuth, then a white precipitate of BiOCl is frequently formed when the first portions of HCl are added to the solution; but this precipitate redissolves when enough dilute HCl is added.

*Complete Precipitation of Group I Out of the Main Sample.*—Take 10 or 15 c.c. of the main solution prepared according to Art. 27 (prepared in this way either by the student, or by the instructor), put it into a small or medium size beaker, and add 3 to 5 c.c. of dilute HCl, stir the mixture, allow the precipitate to settle, then add a drop or two more of HCl to a clear part of the liquid and note whether or not more of the precipitate is formed:—if more is formed, add ½ c.c. more of HCl, stir again, test again to ascertain if enough has been added, and so continue until all of the precipitable cations have been precipitated by means of *the* least amount of HCl. Filter (see figure, Art. 5) and transfer all of the precipitate to the filter. Wash the precipitate *twice*

with distilled water (for details of washing, see Art. 15). Put the collected filtrate and washings into a 500 c.c. Erlenmeyer flask, cork it and label it: "Filtrate from Group I," and set it aside for later use.

### 29. Identification of the Cations in the Group I Precipitate.

By means of a small porcelain spoon, take a small portion of the precipitate from the filter above and put it into a small beaker, add water, heat the mixture to boiling, and filter it through a clean filter; or, if the amount of precipitate is small, pour hot water directly upon the filter on which the precipitate was first collected. Add a drop or two of dilute $H_2SO_4$ to this filtered hot liquid. If a precipitate is obtained, it is $PbSO_4$ formed from the $PbCl_2$ by metathetical reaction. Note that lead chloride is much more soluble in hot water than in cold.

If the "Group precipitate" does not dissolve completely in hot water, then $Hg_2Cl_2$, or AgCl, or both, may be present. To decide if the residue is composed of these substances, put a clean receiver under the last funnel used, and pour ammonia, drop by drop, upon the precipitate on the filter. If the substance on the filter turns black, then $Hg_2Cl_2$ must have been present. If AgCl is present, it dissolves in the ammonia: add an acid (dilute $HNO_3$) to the filtrate until all of the ammonia is neutralized, and if AgCl is present, it will appear as a precipitate. For an explanation of these changes, see Art. 10.

In order to show the foregoing procedure at a glance, it is presented here again in outline form.

Substances on the filter:—AgCl, $Hg_2Cl_2$, $PbCl_2$.

add boiling water

| Filtrate: solution of $PbCl_2$; add dil. $H_2SO_4$. | Residue: AgCl, $Hg_2Cl_2$— add, or shake up with ammonia. | |
|---|---|---|
| Ppt. $PbSO_4$ (white). | Filtrate: acidify with dil. $HNO_3$. Ppt. AgCl. | Residue, if black, indicates Hg. |

Make suitable note book entries of all the results obtained under Arts. 28 and 29.

### 30. Determination of the Cations—Group II.

This group includes all those sulphides which are precipitable from moderately acidified solutions except the cations of Group I. Hence, for the precipitation of this group, we use any solution prepared according to Art. 27 from which the Group I cations have been removed (see end of Art. 28), or from which they are known to be absent—for instance, by the fact that the

original material was changed to *soluble* substances by means of HCl or aqua regia.

*Preliminary Trial to Ascertain if Any of These Metals Are Present.*—Put about 1 c.c. of the proper solution into a test-tube, add 5 drops of dilute HCl, and 2 c.c. of $H_2S$ water. If a precipitate appears, any one or more of the cations $Hg^{++}$, $Pb^{++}$ (small amount only!), $Cd^{++}$, $Cu^{++}$ and $Bi^{+++}$ are present, and they must be precipitated completely out of a larger amount of the sample *as directed below.* In the absence of a precipitate, nothing further need be done with the solution in this article and in Art. 31, and the next trials with it are to be made according to Art. 32.

*Complete Precipitation of Group II Out of the Main Sample.*—Take 10-15 c.c. of the original solution prepared according to Art. 27 in which the cations of Group I are known to be absent, or take all of the filtrate from the precipitation of Group I (see end of Art. 28), put it into the 300 c.c. Erlenmeyer flask suitable for $H_2S$ *gas precipitation* (see Art. 22), add either *dilute HCl* or *water* until the $H^+$ ion concentration is correct (see Art. 17), treat with $H_2S$ gas as directed in Art. 22, and follow the direction in Art. 23 with respect to testing for completeness in precipitating, filtering, and washing the precipitate. The filtrate from which all of the Group II cations have been precipitated is then to be put into a suitable stoppered flask, labeled "Filtrate from Group II," and to be set aside for later use.

### 31. Identification of the Cations in the Group II Precipitate.

Record the color (or colors, if several!) of the precipitate obtained with $H_2S$, together with your inference, from these colors, as to the cations likely to be present. This precipitate may contain HgS, PbS, $Bi_2S_3$, CdS, and CuS. The last four of these react with warm dilute nitric acid, but HgS does not. Hence, to separate the HgS from the others, treat the mixture with dilute nitric acid—for details of operation, see Art. 22. If the precipitate is completely disintegrated, then HgS is absent, but if a residue remains, $Hg^{++}$ may be present. In either case, the clear liquid is to be put in a clean beaker or dish, 1 c.c. of conc. $H_2SO_4$ is to be added, and the liquid is to be evaporated as far as possible on a large beaker full of boiling water (a water bath), or some corresponding heating apparatus.

If a residue that might be HgS has been left by the nitric acid treatment, it should be treated as in Art. 22, while the preceding evaporation is under way:—this procedure will show whether or not $Hg^{++}$ is in the sample under consideration.

To the residue (small bulk!) from the nitric acid evapora-

tion above, add a little water, stir the mixture, and try to ascertain whether or not a small amount of white powder—($PbSO_4$)—is present:—This reveals itself if the vessel is given a circular motion so that the liquid rotates in the vessel. Of course, if lead has been recognized in the first group of cations, it need not be recognized again here. In some samples, however, the quantity of lead is too small to give a precipitate of $PbCl_2$, hence it should be looked for here.

The next step in the search of the other cations that might be present in *this solution* ($Bi^{+++}$, $Cu^{++}$, $Cd^{++}$), is the addition of *excess* (?) of ammonia to the whole sample under consideration. In the presence of an excess of ammonia, $Cu^{++}$ and $Cd^{++}$ form soluble compounds, but $Bi^{+++}$ is precipitated as $Bi(OH)_3$. This precipitate should be white. If $Cu^{++}$ is present, the solution will be deep blue. Collect the $Bi(OH)_3$ on a filter, but keep the filtrate for further use as directed below. Wash the $Bi(OH)_3$ precipitate, then drip dilute HCl upon it, and let the resulting drops of solution fall into a large beaker of distilled water. The HCl changes the $Bi(OH)_3$ to $BiCl_3$ as long as the concentration of the $H^+$ ion is great; but when, by dilution with water, the $H^+$ ion concentration is made very small, the *reverse* change takes place,—namely, $H_2O$ and the salt $BiCl_3$ react to form HCl and the basic salt BiOCl, as per following equation:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

Of all the common metal ions here considered, $Bi^{+++}$ is the only one that has this property. This reaction is known as *hydrolysis:* it is the reverse of the reaction between an acid and a base. All salts of weak acids or of weak bases undergo slight hydrolysis when they are dissolved in water.

We must now return to the liquid in which $Cd^{++}$ and $Cu^{++}$ may be contained—i. e., the liquid to which an excess of ammonia had been added and which may have been filtered to remove a precipitate of $Bi(OH)_3$. If this solution is colorless, then it is free from $Cu^{++}$, and it may be tested immediately for $Cd^{++}$ by means of $H_2S$ water (yellow ppt., CdS). If the solution is blue, secure a freshly prepared solution of potassium cyanide (care! poison! do not get it on your hands or breathe its fumes), and while stirring or shaking the mixture, add—*drop by drop*—the *least* amount of potassium cyanide with which the blue color will disappear. Then add $H_2S$ water.

A yellow precipitate (CdS) shows the presence of $Cd^{++}$.

The potassium cyanide reacts with $Cd^{++}$ salts as follows:

First, $Cd(CN)_2$ is formed by metathesis—

$$CdCl_2 + 2KCN = Cd(CN)_2 + 2KCl.$$

Second, $Cd(CN)_2$ unites with 2KCN to form a double cyanide, $(KCN)_2Cd(CN)_2$.

To show the main ions of this resulting double cyanide of potassium and cadmium, its formula is written thus:— $K_2Cd(CN)_4$. It ionizes primarily into $2K^+$ and an anion composed of $Cd(CN)_4^{--}$. The latter ionizes further,—into $Cd^{++}$ and $4CN^-$. This takes place only to a slight extent, yet sufficiently so that a precipitate of CdS is formed when $H_2S$ is added.

The potassium cyanide reacts with $Cu^{++}$ as follows:

First, $Cu(CN)_2$ is formed by metathesis—

$$CuCl_2+2KCN=Cu(CN)_2+2KCl.$$

Second, the cupric cyanide dissociates into cuprous cyanide and free cyanogen—

$$2Cu(CN)_2=2CuCN+(CN)_2.$$

Third, cuprous cyanide unites with 3KCN to form the double cyanide $K_3Cu(CN)_4$. The secondary ionization of the latter, which gives $Cu^{++}$ ions, does *not* take place sufficiently so that CuS may be formed when $H_2S$ is added (difference from $Cd^{++}$!).

Make note book entries of the results obtained according to Arts. 30 and 31.

The following table presents the following directions in outline:

Sulphides precipitated from slightly acidified solutions by $H_2S$: HgS, PbS, $Bi_2S_3$, CuS, CdS;

boil with dil. $HNO_3$.

| | | |
|---|---|---|
| Residue: HgS—treat with conc.HCl and add a little $KClO_3$, boil off excess of chlorine, dilute with water and add $SnCl_2$. | Solution: Pb $(NO_3)_2$, Bi $(NO_3)_3$, Cu $(NO_3)_2$, Cd $(NO_3)_2$; add a little conc. $H_2SO_4$ and evaporate to small bulk—add $H_2O$. | |
| Ppt. gray, Hg: white, HgCl. | Ppt. $PbSO_4$. | Filtrate: salts of Bi, Cu, and Cd: add $NH_4OH$ to slight excess. Deep blue color indicates copper. |
| | Ppt. $Bi(OH)_3$. Dissolve by dropping HCl upon the ppt. on the funnel and allow solution to run into a large volume of water—ppt. BiOCl. | Filtrate: salts of Cu and Cd. Add KCN drop by drop till solution is colorless—then add $H_2S$,—ppt. CdS, yellow. |

**32. Determination of the Cations—Group III.**

This group includes all the metals precipitated out of a solution prepared according to Art. 27 when (1) the solution is rendered alkaline with ammonia (plus $NH_4Cl$) and when (2) $(NH)_2S$ is then added to the mixture, *provided* that the cations of *Group I* and of *Group II* are either known to be *absent* or have been *removed*. The precipitate thus obtainable may consist of:— $Al(OH)_3$, $Fe(OH)_3$, $Fe_2S_3$, NiS, FeS, MnS, and ZnS.

*Preliminary Trial to Ascertain the Presence or Absence of Cations of Group III.*—Put into a test-tube about 2 c.c. of the

original solution prepared according to Art. 27 if Groups I and II are known to be absent, or of the filtrate obtained after removing them completely (see last part of Art. 30 or of 28, respectively); add 1 c.c. of $NH_4Cl$ solution, 1 c.c. of ammonia, and a few drops of ammonium sulphide solution, shake the mixture vigorously, and note whether or not a precipitate is formed. Note the appearance of the precipitate, and infer from it what cations may be present:—enter your inference in the note book.

*Precipitation of Group III.*—Secure the main portion of the solution of which a part has just been tested, add $NH_4Cl$ solution to it to the extent of one-fourth (or more?) of the volume of the sample, then add ammonia to it in small portions until, after shaking, the mixture turns red litmus blue, and then, if necessary (?), add ammonium sulphide solution in very small portions until after shaking, the further addition of a small amount of ammonium sulphide produces no further precipitate. Filter the mixture carefully, transferring all of the precipitate to the filter paper, and collecting the filtrate in a clean flask. Close this with a stopper, label it: "Solution for Art. 34," and set it aside. *Immediately* after the solution has drained completely out of the funnel, fill the filter with water to wash the precipitate, but do not keep the washings—i. e., do *not* add them to filtrate from the original solution. When the filter has drained empty again, fill it again with water to wash the precipitate a second time. It may then be considered that the dissolved material in the original mixture has been washed out of the precipitate. Proceed immediately to treat the precipitate as per following paragraph.

**33. The Identification of the Cations in the Group III Precipitate.**

Put a clean receiver (beaker or flask) under the funnel which holds the Group III precipitate, and pour dilute HCl drop by drop upon the precipitate on the filter, or if the quantity of precipitate is large, remove a portion with a small porcelain spoon, put it into a small beaker, add 2-5 c.c. of dilute HCl, stir the mixture thoroughly, and if an insoluble portion remains, filter the mixture through a clean filter. All of the substances possibly present except NiS will dissolve in the HCl. Test the residue on the filter according to the second paragraph below. Put five drops of dilute $HNO_3$ into the clear solution just obtained, pour it into a small dish, place this on a "water bath" and allow the liquid to evaporate.

In the meanwhile, proceed to test the residue on the filter above to ascertain if it is really a compound of $Ni^{++}$. Secure a piece of platinum wire, clean the end carefully, bend it into a circular loop of about $\frac{1}{8}$-inch diameter, heat it to incandescence

in the flame, dip it, while *hot,* into some powdered sodium metaphosphate ($NaPO_3$) or into some microcosmic salt, and hold the mass in the center of the upper third of a Bunsen flame (the hottest part). The salt should melt and form a *clear colorless drop* in the loop of the wire. If necessary, pick up more of the salt with the heated end, but do not attempt to make too large a "bead" because it drops off too easily when hot. Next, bring the hot bead in contact with some of the residue on the filter, and heat the bead again until it fuses. Care must be taken *not* to pick up so much of the solid as to make the bead opaque after it is fused again. If the latter has happened, the bead should be removed by fusing it and "throwing" it away, and a new bead should be made. If the amount of residue on the filter is very slight, tear off a small piece of the paper with the residue on it, stick it to the bead and put the whole mass in the flame. The components of the paper form nothing but $CO_2$ and $H_2O$ on combustion, and hence nothing is left in the bead except the "residue." With a suitable amount of *Ni* compound, the bead will be transparent with a reddish brown color. In order to become familiar with the color due to nickel, a bead should be made with a *known* nickel salt.

In the meanwhile, the solution on the water bath will have been evaporated to dryness. Dissolve the residue in a very small amount of water (2.5 c.c.), pour the solution into a test-tube, and add 5 c.c. of sodium hydroxide solution from the reagent bottle on the desk. Stir the mixture vigorously, and if it is "thick" with precipitate, add a little water plus an equal amount of sodium hydroxide solution to *thin* it. If a precipitate (not merely a "cloudiness") is present, filter the mixture: if the filter paper is *attacked* by the solution, dilute it to double its volume with water. Divide the liquid into two parts: to one part add an equal volume of $NH_4Cl$ solution; and stir the mixture:—if $Al^{+++}$ is in the sample under consideration, $Al(OH)_3$ should be obtained here. To the other part of the solution, add some $H_2S$ water: if $Zn^{++}$ is in the sample, white ZnS should be obtained here. If a precipitate has been removed above from this liquid by filtration, and it has a red or brown color, transfer a very little bit of it with a spoon to a dish, put a few drops of dilute HCl on it to dissolve it, and add a few drops of potassium ferrocyanide:—if a *deep-blue* color is formed in the mixture, iron is present in the sample. Take another small portion of the precipitate on the last filter (or a bit of the filter with the precipitate on it) and put it into a clean porcelain crucible, put the crucible on a clay-covered triangle, and the whole on the ring of a ring-stand *in position to be heated with a burner,* warm the crucible gently to dry the precipitate, then put a few "pinches" of powdered $NaKCO_3$ and $KNO_3$ on the precipitate, and turn the

full heat of the burner on the crucible until the mass melts:—if $Mn^{++}$ is in the sample, the fused mass will have a green color when it is cold. To clean the crucible put the cold crucible in water to "soak" out the fused mass.

Make suitable entries in your note book concerning the results obtained in this paragraph.

The following table presents the contents of this article 33 at a glance.

THE "SEPARATION" OF GROUP III.

The precipitate may contain:—$Al(OH)_3$, $Fe_2S_3$, NiS, FeS, MnS, ZnS.

treat with cold dil. HCl.

| Residue: test with borax bead, if reddish brown, Ni is indicated. | Filtrate: $MnCl_2$, $FeCl_2$, $ZnCl_2$, and $AlCl_3$: add dil. $HNO_3$, and boil, thus removing $H_2S$ and oxidizing Fe if present. Evaporate to small bulk. Add NaOH solution, stir and dilute with water. | |
|---|---|---|
| | Ppt. $Mn(OH)_2$, $Fe(OH)_3$.<br>(a) Fuse a portion with $NaKCO_3$ and $KNO_3$—green color indicates Mn.<br>(b) Dissolve another portion in dil. HCl and add potassium-ferrocyanide: deep blue ppt. indicates Fe. | Filtrate: $Na_2ZnO_2$, $Na_3AlO_3$.<br>(a) Treat a portion with $H_2S$: ppt. ZnS (white).<br>(b) Acidify another portion with HCl and add ammonia:—ppt. $Al(OH)_3$. |

A brief explanation will now be given of the reactions in the foregoing operations in this article.

(a) The HCl added to dissolve the whole Group III precipitate reacts metathetically with all substances except NiS.

(b) The reactions in the formation of the "nickel bead" are the following:—

$$NiS+3O \text{ (from the air)} = NiO+SO_2$$

$$NiO+NaPO_3=NaNiPO_4 \text{ (phosphate of two cations!)}$$

This phosphate is dissolved by the molten $NaPO_3$, and makes a "colored glass."

(c) When the HCl solution of all metals except Ni is treated with $HNO_3$, the $H_2S$ and any ferrous salt present are "oxidized" according to the following equations:

$$3H_2S+2HNO_3=3S+4H_2O+2NO.$$

$$3FeCl_2+HNO_3+3HCl=3FeCl_3+NO+2H_2O.$$

(d) The NaOH acts on the different metal compounds as explained in Art. 3.

(e) When $Fe(OH)_3$ is dissolved in HCl and treated with potassium ferrocyanide, a metathetical reaction takes place:—

$$4FeCl_3+3K_4Fe(CN)_6=12KCl+Fe_4[Fe(CN)_6]_3,$$

Prussian Blue!

(f) When the $Mn(OH)_2$ is fused with $NaKCO_3$ and $KNO_3$, the following reaction takes place:—

$$Mn(OH_2 + 2O + NaKCO_3 = NaKMnO_4 + H_2O + CO_2$$
$$(KNO_3) \qquad \text{a manganate!}$$

(g) When $H_2S$ is passed into an alkaline solution of a zinc salt, a metathetical reaction takes place:—

$$Na_2ZnO_2 + H_2S = 2NaOH + ZnS.$$

(h) When ammonium chloride is added to a solution which contains $NaAlO_2$, the *total* effect produced is the same as it would be if the two substances from which it is formed (HCl and $NH_4OH$) were added separately. HCl would act as explained in Art. 4 (b) and ammonia would then react as follows:—

$$AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl.$$

The two reactions together would be expressed in *one* equation as follows:

$$NaAlO_2 + NH_4Cl + 2HOH = NaCl + Al(OH)_3 + NH_4OH.$$

**34. The General Plan of the Determination of the Cations of Group IV.**

This group includes all the alkaline earth metals and magnesium. The cations of all the three previous groups have been removed from the original solution by the procedures given in Arts. 28, 30, and 32; and the solution, hence, should contain only members of Groups IV and V (i. e., the ions $Ca^{++}$, $Sr^{++}$, $Ba^{++}$, $Mg^{++}$, $Na^{+}$, and $K^{+}$). The solution containing these ions is—

(a) The filtrate from Group I (if II and III are absent); see end of Art. 28.

(b) The filtrate from Group II (if III is absent); see end of Art. 30; or

(c) The filtrate from Group III, marked "Solution for Art. 34"; see end of Art. 32.

(d) The original solution (if Groups I, II, and III are absent).

The barium, calcium, and strontium ions are to be determined by means of the spectroscope (see Art. 35 for details) and the magnesium ion is to be precipitated, *after the removal of the calcium, strontium, and barium ions,* as magnesium ammonium phosphate ($MgNH_4PO_4$) according to the procedure outlined in Art. 36. The removal of *all the* metal ions except $NH_4^{+}$, $Na^{+}$, and $K^{+}$ before the magnesium is determined as phosphate is necessary because *all* form insoluble phosphates (see table of solubilities of Acids, Bases, and Salts, Chapter VI).

**35. The Flame Colorations and Spectra of $Ca^{++}$, $Sr^{++}$, $Ba^{++}$, $Na^{+}$, and $K^{+}$.**

Vapors of compounds of these metals become incandescent at the temperature of the Bunsen flame, and the metals may be rec-

ognized from the colors that they impart to the flame. There are only two other common metals ($Cu^{++}$ and $Pb^{++}$) which color the flame under similar conditions. But the two metals have been removed in Groups I and II, and hence do not affect the determinations in this group. A list of the flame colors is given below:

| | |
|---|---|
| Brick red—Calcium. | Yellow—Sodium. |
| Bright red—Strontium. | Bluish-green—Copper. |
| Green—Barium. | Pale blue—Lead. |
| Violet—Potassium. | |

Since the colors from some metals "hide" or obstruct the colors from others, it is necessary, with mixtures containing several of these metals, to view the colored flame through a spectroscope. The prism in the spectroscope resolves the light from these incandescent vapors into their "primary" colors or components. These components are relatively few in number, and each one is of a very definite color, hence the spectra of the incandescent vapors of these metals appear as spots of light at particular points in the whole *range* of possible colors, or since the light is admitted through a *slit*, *lines* of these different component colors are obtained at particular points in the "range" of the sunlight's spectrum. Several metals may throw their light simultaneously through the same prism without interfering with each other, and the characteristic lines of each metal will show at their proper places simultaneous with the lines of the other metals at their proper places. The lines never overlap, and hence mixtures of these metals are thus "analyzed" at a glance.

A chart giving the positions and colors of the lines characteristic of the metals $Ca^{++}$, $Sr^{++}$, $Ba^{++}$, $Na^{+}$, and $K^{+}$ should be found near the spectroscope for ready reference, and in case of doubt the analyst should secure a salt of the metal in question and produce its spectrum. A comparison with this known spectrum will aid to identify the unknown.

*Manipulation for the Flame or Spectroscope Test.*—Clean a platinum wire mechanically as thoroughly as possible, then hold it in the flame of a Bunsen burner to see if it imparts any color to the flame. If it does, it requires further cleaning, which is accomplished by dipping it into concentrated hydrochloric acid and heating it in the flame and repeating this treatment until the glowing wire imparts no color to the flame. Now moisten some of the sample with dilute hydrochloric acid, dip the wire into it, and hold it in the flame. Any color imparted to the flame indicates the metal placed with the color in the list above.

Viewed through the spectroscope, these flame colors present the following component colors:

*Sodium*, a yellow line—which is usually used to adjust the

"scale":—the prism should be moved until a certain number on the scale—say, 10 or 50—is at the sodium line. The positions of the lines of other metals are usually given with reference to the sodium line.

Sodium compounds are so widespread in nature that almost all substances contain enough sodium to give the sodium line when heated in the Bunsen flame; but sodium is not to be considered as present unless enough of it is present to color the flame heavily and persistently.

*Potassium*—a deep red line to the left of the sodium line—(at 7.9 or 17).

*Calcium*—two very broad and heavy lines, close to the sodium line; green to the right and red to the left of sodium. Several other light red and green lines are also present.

*Strontium*—several heavy (and several light) red lines (to the left of sodium), the number of which is greater than the red lines of calcium.

*Barium*—several heavy (and several light) green lines (more than for calcium) and also a few light red lines.

**36. The Identification of the Cations of Group IV.**

(a) *To identify the $Ca^{++}$, $Sr^{++}$, and $Ba^{++}$ ions,* proceed as follows: Clean a platinum wire as described in Art. 35, dip it into the solution for Group IV (as described in (a), (b), and (c) of Art. 34 and test for both flame coloration and spectroscopic lines. Be careful to obtain a *very positive* test for these ions ($Ca^{++}$, $Sr^{++}$, and $Ba^{++}$) before reporting them. It may be necessary to evaporate the solution you are testing to smaller bulk, in order that the concentrations of these ions may be larger.

(b) *The removal of the $Ca^{++}$, $Sr^{++}$, and $Ba^{++}$* ions: In order to identify the $Mg^{++}$ ion, it is necessary to remove the $Ca^{++}$, $Sr^{++}$, and $Ba^{++}$ ions from the solution, if the spectroscope has proven them to be present. (See again last part of Art. 34.) To do this, proceed as follows: The solution must contain $NH_4Cl$ and enough $NH_4OH$ to turn red litmus blue (the $NH_4Cl$ must be present to prevent the precipitation of the $Mg^{++}$ as $Mg(OH)_2$). If these substances are not present in the solution, they must be added in proper amounts. Then put the mixture into a small flask or beaker, heat it to boiling, and keep it boiling while adding the following reagents drop by drop until, in clear portions of the liquid, additional drops produce no more of the precipitate:

(a) If $Ba^{++}$ or $Sr^{++}$ is present, add ammonium sulphate solution, $(NH_4)_2SO_4$;

(b) If $Ca^{++}$ is present, add ammonium oxalate solution, $(NH_4)_2C_2O_4$;

(c) If $Ba^{++}$ and $Ca^{++}$, or $Sr^{++}$ and $Ca^{++}$, are present, add *first* ammonium sulphate, in sufficient amount (?), and then ammonium oxalate in sufficient amount (only a little of the latter will be needed!) Precipitates of $BaSO_4$ or $SrSO_4$, and of $CaC_2O_4$ are formed by metathetical reaction.

Allow the precipitate to settle, but do not allow the liquid to cool! If it has been boiled enough, the precipitate will settle rapidly, and afterwards will not pass through the filter. Decant the clear liquid upon a clean filter paper, and collect the filtrate in a clean small flask. Add another drop of the reagents just used to ascertain if all the alkaline earth cations have been precipitated.

(c) *The Determination of Magnesium.*—To the liquid obtained in (b) add 2-5 c.c. of sodium phosphate ($Na_2HPO_4$), cool the liquid if it is still warm (by allowing the tap-water to flow over the outside of the flask); close the flask with a stopper, and shake vigorously until a dense, crystalline (not flocculent!) precipitate appears. Sometimes 3-5 minutes of shaking are necessary. If a precipitate with the *correct appearance* is obtained, $Mg^{++}$ is present in the sample under consideration. The precipitate is formed by metathetical reaction:—

$$MgCl_2+NH_4OH+Na_2HPO_4=MgNH_4PO_4+2NaCl+H_2O.$$

Filter this precipitate off, saving the filtrate and mark it "Solution for Art. 37."

The following table presents the foregoing directions in outline:—

THE "SEPARATION" AND IDENTIFICATION OF GROUP IV.

The filtrate from the procedures of Arts. 28, 30, or 32 may contain $Ba^{++}$, $Ca^{++}$, $Sr^{++}$, $Mg^{++}$ (and members of Group V).

| | |
|---|---|
| Make flame and spectroscopic tests on concentrated solution for $Ba^{++}$, $Sr^{++}$, and $Ca^{++}$. | Remove the $Ba^{++}$, $Sr^{++}$, and $Ca^{++}$ by means of $NH_4Cl$ $NH_4OH$, $(NH_4)_2SO_4$, and $(NH)_2C_2O_4$. Filter off the precipitates of $BaSO_4$, $SrSO_4$, and $CaC_2O_4$. |
| | To this filtrate add $Na_2HPO_4$ solution: a dense crystalline precipitate (after 3-5 minutes shaking) indicates $Mg^{++}$. |
| | Filter and save filtrate for Group V. |

**37. The Identification of Group V.**

The solution obtained in Art. 36, labeled "Solution for Art. 37," may contain $Na^+$ and $K^+$. In this procedure these will not be separated, as is often done, but they will be identified by spectroscopic tests, made according to the procedure of Art. 35.

In the identification of the cations of Group IV. the ions $Na^+$ and $K^+$ may have been determined along with the others. If *posi-*

*tive* tests have been obtained for $Na^+$ and $K^+$, it is not necessary to identify them again here. If, however, they have *not* been determined, the solution should be evaporated to small bulk (practically to dryness); and the spectroscopic test for $Na^+$ and $K^+$ made.

Great care should be exercised in the determination of $Na^+$: even very small amounts (from the air, etc.) will give tests for sodium, and hence only a *very prominent* sodium line should be taken to indicate the presence of $Na^+$.

The test for $NH_4^+$ should *only* be made on the ORIGINAL unknown solution handed you, for its presence at the end of our qualitative procedure would mean nothing since ammonia and ammonium salts have repeatedly been added to our solution as reagents. The *original* solution should be tested in the following manner:

Put a pinch of the original dry sample (or solution) into a test-tube, add a few drops of sodium hydroxide solution, and warm the mixture. If ammonium compounds are present, the mixture will emit the odor of ammonia,—produced according to the equations:

$$NH_4X + NaOH = NH_4OH + NaX$$
$$NH_4OH = NH_3 + H_2O$$

The following table presents the procedure in outline:

THE IDENTIFICATION OF GROUP V.

| | |
|---|---|
| Evaporate solution to small bulk; make spectroscopic tests for $Na^+$ and $K^+$ according to procedure of Art. 35. | Original unknown sample is treated with NaOH: an odor of ammonia proves presence of $NH_4^+$. |

**38. Determination of the Anions.**

As mentioned in Art. 26, this procedure has been designed merely for the following compounds of the common metals: oxides, sulphides, carbonates, phosphates, nitrates, acetates, sulphates (except the insoluble sulphates) and chlorides (except AgCl). The procedure in Arts. 28-37 enables us to ascertain what metals are present in a substance to be analyzed, but when the substance is not merely a metal (or an alloy), but a compound, it is necessary to ascertain what the metals are compounds of. The first thing that gives a clue to the nature of these compounds is their solubilities:—this knowledge together with a knowledge of the cations in the compound enables the analyst to make certain conclusions concerning the possible nature of the compound. Thus if the substance is soluble in water and contains the cations $Ca^{++}$ and $Ba^{++}$, then it cannot be a sulphide, oxide, carbonate, phosphate or sulphate; and only the nitrate, chloride, and acetate ions should be tested for.

Only "water-soluble" compounds should be tested for the nitrate ion, acetion, sulphate ion and chloride ion according to the special

directions given below. Since such "water-soluble" substances may also be sulphides, carbonates, or hydroxides, it is necessary to note in connection with these other tests (1) if *much* of an acid is necessary to render the solution acid to litmus (presence of hydroxides), or (2) if a gas is evolved when an acid is added ($H_2S$— or $CO_2$).

If the substance is an insoluble sulphide, it will either evolve $H_2S$ when treated with an acid, or solid sulphur will be formed. If it is a carbonate, it will effervesce when treated with an acid but the gas evolved will be odorless and colorless.

Any "water-soluble" substance which dissolves "in acids" *without the evolution* of a gas or without the formation of sulphur, should be either an oxide or a phosphate because nothing else is to be given to the student in this work. But this holds also for all substances of common occurrence. Such substances should be tested for the phosphate ion by method (b) given below. If it is thus found not to be phosphate, then it must be an oxide.

**39. Special Tests for Anions.**

*The Sulphur Ion.*—Acidify the original aqueous solution with a few drops of dilute hydrochloric acid and add a few drops of barium chloride solution. No other anion gives an insoluble barium salt under these conditions.

*The Nitrate Ion.*—To the original aqueous solution add an equal volume of concentrated sulphuric acid and allow the mixture to cool. Then pour *carefully* upon it a solution of ferrous sulphate in such a manner that the solutions will not mix, the ferrous sulphate solution being on top. A brownish-black ring ($FeSO_4$:NO) at the boundary of the two solutions indicates the presence of a nitrate.

*The Chloride Ion.*—Acidify the original aqueous solution with dilute nitric acid and add silver nitrate solution: a *white* precipitate indicates the presence of a chloride; if the precipitate has a slight yellow color, it may indicate the presence of a bromide; and if the precipitate is tinged deep yellow, it may indicate the presence of an iodide.

If either of the last two substances is thus indicated, it becomes necessary to make use of special directions, to be obtained from the instructor, to test for the presence or absence of the chloride ion.

*The Phosphate Ion.*—(a) If the sample is soluble in water, it may be tested for phosphates by adding ammonium chloride, ammonium hydroxide and magnesium chloride. A dense, crystalline, white precipitate (of $MgNH_4PO_4$) indicates the presence of phosphates.

(b) If the sample is *not* soluble in water but has been dis-

solved by means of acids, the phosphate ion must be tested for in the following manner: dissolve the solid in dilute nitric acid, pour about one cubic centimeter into a clean test-tube, warm it to "blood heat," then add from two to three cubic centimeters of ammonium molybdate to the hot solution, and then let it stand for about five minutes. A yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4(MoO_3)_{12}$ indicates the presence of a phosphate.

*The Carbonate Ion.*—Place some of the original solid or aqueous solution into a test-tube and add a small quantity of dilute hydrochloric acid. If considerable quantities of gas are evolved, the gas should be tested by suspending a drop of clear calcium hydroxide or barium hydroxide solution from the end of a glass tube in the upper part of the test-tube. A white cloudiness (of $CaCO_3$ or $BaCO_3$) in the suspended drop indicates the presence of a carbonate.

*The Acetate Ion.*—(a) Add a few drops of a dilute, slightly acidified solution of ferric chloride (the stock solution of ferric chloride contains the proper amount of acid) to a little of the original solution: a reddish coloration indicates the presence of an acetate. On boiling this solution, a reddish-brown precipitate of ferric hydroxide is usually obtained; sometimes a deep reddish-brown solution results.

If a phosphate is present, a light yellow precipitate will be formed at once in the cold and *not* a reddish solution. If a carbonate is present, a reddish-brown flocculent precipitate will be formed at once in the cold, but *not* a reddish solution. To remove the carbonate so that it does not interfere with the acetate test, proceed as follows: to the original solid or solution add dilute hydrochloric acid drop by drop until, upon warming, carbon dioxide is no longer evolved. Care should be taken not to make the solution but very slightly acidic. Then add a few drops of ferric chloride solution. A reddish solution indicates an acetate.

(b) Add to the original dry sample a mixture of equal volumes of concentrated sulphuric acid and of alcohol. Stir and warm the mixture: a *fruity* odor indicates the presence of an acetate. Only pure alcohol should be used in making this test or the *fruity* odor will be obscured. This test requires considerable training and technical ability.

**40. Conclusion.**

After examining a substance in accordance with the directions in Arts. 27 to 39, inclusive, a definite conclusion should be reached by the student concerning the nature of the substance as a whole, and he should look into some large text-book for a description of the compound to confirm his conclusion. The compounds given

the student should be important in themselves—as a whole. They should be commercially important salts or natural compounds (minerals), and the student should strive to make himself familiar with their appearances and uses.

### Questions on Chapter X.

1. (a) In what respect does a solution of hydrogen sulphide in water, which contains also some of a strong acid, differ from a solution of hydrogen sulphide which contains no strong acid? Explain or discuss this difference adequately.

(b) When a solution of hydrogen sulphide in water is added to a pure zinc sulphate solution, a precipitate is obtained; but when some of a strong acid is first added to the zinc sulphate solution and then the hydrogen sulphide solution is added, no precipitate is obtained: point out definitely why a precipitate is obtained in the first case and none in the second.

(c) A solution of a copper salt will give a precipitate when pure hydrogen sulphide solution is added to it and also when a hydrogen sulphide solution which contains some of a strong acid is added to it (or when some of a strong acid is first added to the copper salt solution and then the hydrogen sulphide solution is added): point out why the copper salt solution behaves different from the zinc salt solution in the instances just cited.

2. A druggist discovered that his stock of alum (a double sulphate of aluminium and potassium) had been contaminated with Epsom salt (magnesium sulphate): name a general reagent with which the aluminium and the magnesium may be separated from a common solution and secured in two separate portions; and describe how to do this. Write all questions for the metathetical reactions occurring in this work.

3. Name another common reagent which may be used with the solution of the two substances in question 2.

4. Make an outline of the separation of Group III in the procedure for the analysis of metals.

5. Give the equation for the precipitation of magnesium in the scheme for the determination of metals. Why does one hydrogen atom appear in the formula of the substance commonly designated as sodium phosphate? Why is aluminium sulphide not obtained when an aluminium salt is treated with a sulphide?

6. Describe briefly how to test an unknown to determine if it is a sulphate. Would you make this test on a substance which is insoluble in water? Name the reagent that is used to test an unknown to ascertain if the latter is a phosphate in case this unknown is insoluble in water.

7. (a) Calcium phosphate is given out as an unknown to be analyzed. State by what means it will be dissolved and give

the equation for the reaction which takes place during the dissolution of this substance.

(b) As this solution is taken through the regular course of analysis, where will the calcium be precipitated? Explain as fully as possible why it is precipitated at this point instead of at the usual place.

8. An unknown consists of water soluble salts of copper and of cadmium: describe all that will occur as this solution is worked with in accordance with the direction for the determination of the cations, being careful to describe the color or general appearance of all the precipitates or anything that may be seen. Finally write all equations occurring in this work that you are prepared to write, and for the remaining reactions state the composition of the main substances formed.

9. The composition of a yellow powder—which is either an oxide or a salt of a common metal—is to be determined: this substance is found to be insoluble in water; hydrochloric acid acts upon it but does not convert it to soluble substances; while dilute nitric acid dissolves it readily. The procedure for the determination of the cation shows that in Groups I and II only lead is present.

(a) State, in their order, very briefly and definitely, the results this solution will give while it is examined according to the directions for both the first and the second group. Before answering this, read (b).

(b) You should end the procedure in the first and second group as soon as you have experimental indications that the rest of the procedure is unnecessary; state what experimental result induces you to discontinue the procedure of Group I. Do the same for Group II, being particularly careful to give all your reasons here.

(c) Why does this solution give a precipitate in Group II? What is the color and quantity of this precipitate?

(d) Besides giving the precipitate in Group II, this solution may turn milky white; what is the substance that makes this solution white; what two substances act upon each other to produce this "white" substance?

(e) In general, the unknowns that you are to analyze may contain the metals in one of the following *forms:* as a free metal or alloy, as an oxide, as a nitrate, chloride, sulphate, acetate, carbonate, sulphide, or phosphate. Judging from its behavior above, in which of these forms may the lead in this sample be present? Give your reasons why it could not be in the forms excluded. The yellow powder is litharge, PbO, a commercially important substance.

10. In what respect does a solution of ammonia which contains also some of an ammonium salt differ from an ammonia

solution which contains an ammonium salt? Explain or discuss this difference at length to show what you know about it.

(b) When pure ammonia solution is added to a magnesium sulphate solution, a precipitate is obtained: but when an ammonia solution which contains also some of an ammonium salt is added to a megnesium sulphate solution, no precipitate is obtained: point out definitely why a precipitate is obtained in the first case and none in the second.

(c) A solution of an aluminium salt will give a precipitate when pure ammonia solution is added to it and also when an ammonia solution containing some of an ammonium salt is added to it; point out why an aluminium salt solution behaves different from a magnesium salt solution in the instances just cited.

11. Brass is an alloy of copper and zinc. By what means would you produce soluble compounds of these metals from brass? From this solution either one or both of these metals may be precipitated separately by means of two very common reagents: name one of these reagents and state what you must do to secure the two metals in two separate portions. Finally, change the copper to copper nitrate and then change as much of the zinc as possible to zinc chloride. Write all equations for the metathetical reactions occurring in this work.

12. Name the other of the two common reagents which may be used in the solution in question 11 to separate copper from zinc out of the above solution and proceed with the use of this reagent to do again what is called for in question 11.

13. Make an outline of the separation of the common metals into the usual groups; give the formulæ of all the precipitates in each precipitated group; and give the equation for the precipitation of one metal in each of the "precipitated" groups.

14. Enumerate all the facts made use of in the analytical outline to reveal the nature of bismuth or to test for it. In the last test for bismuth, what reaction occurs? What is the name of this sort of a reaction? Point out the origin of the name. What substance must be present in the solution in order to prevent this reaction in the case of bismuth? Present this matter as fully as you can.

15. What observations and what additional tests would enable you to decide that a substance is a carbonate? If an unknown compound soluble in water has been found to be a compound of copper, what common anions would you test for? Why for these only? Describe briefly how to test for chlorides. Describe briefly how to test for nitrates.

## CHAPTER XI.

## ELECTROLYSIS—THE CHEMICAL CHANGES AT THE POLES OF ELECTROLYTIC CELLS.

NOTE.—Since in connection with the study of the preceding chapter on qualitative analysis it may be desirable to spend a considerable number of hours in the laboratory on "unknowns," it is advisable to present the following chapters (Chapters XI and XII) in the class room. It will be found that most of the experiments can best be performed on the lecture table instead of having the students perform them in the laboratory.

### 1. Electrolysis.

Electrolysis is the chemical decomposition of substances by means of a direct electric current. The latter must naturally be forced through the electrolytic cells by some outer agency, such as a battery or a dynamo.

### 2. The Algebraic Signs of Poles.

An *electrolytic cell* has its poles marked in accordance with the kind of electricity sent *into* it. The negative pole is also called the *cathode,* because the cations move toward it while the current passes, and the *positive* pole is also called the *anode* for the corresponding reason.

A battery cell or a dynamo (which supplies current) has its poles marked in accordance with the kind of electricity which it supplies. Thus, the positive poles of a battery cell or a dynamo is that pole at which positive electricity flows out of it. When this pole is connected with a wire to the pole of an electrolytic cell, the latter is made the positive pole, because positive electricity is sent into it at this point.

The difference in the assigning of signs to the poles of battery and electrolytic cells, respectively, corresponds to the difference in our use of these cells:—the battery cells are used to *supply* current and the poles are marked to show *what they supply;* while electrolytic cells are cells into which we send current to produce results, and their poles are marked to show *what we send into* them.

### 3. The Electrolysis of a Solution of Zinc Chloride.

**Experiment.**—Secure a liter-beaker full of an (approximately) 10 per cent solution of $ZnCl_2$. Suspend a strip of sheet brass about 2 inches wide and 8 inches long into it on one side, and dip into it a carbon pole prepared as follows: A piece of wide glass tubing about $1\frac{1}{2}$ inches wide and

10 inches long is fitted with a rubber stopper with two holes, one for an electric light carbon or a similar graphite rod, and the other for a piece of narrow glass tubing. Let the graphite rod extend into the tube almost to its other end. Trim the end of the carbon rod projecting outside of the tube so as to leave a flat strip of the width of the carbon rod and about $\frac{1}{8}$ inch in thickness. With the aid of "burette screw clamp," the end of a copper wire for the electrical connection is clamped to this flat end of the carbon rod. Secure a narrow glass tube about 24 inches long, bend it twice at a right angle so that when everything is properly assembled this narrow glass tube may extend from the under surface of the stopper over the edge of the beaker to the bottom of a bottle or cylinder standing beside the beaker. The latter should serve to collect the chlorine gas which is to be evolved: Secure such a vessel and put a wad of cotton in its neck. This will serve to prevent the chlorine from escaping into the room. Secure a suitable source of direct electric current with an electric pressure of 8 to 12 volts. Connect the brass strips to the negative pole of this "current source" and the carbon rod to the positive pole, thus making the brass rod the negative pole and the carbon rod the positive pole of the electrolytic cell. When connection is made so as to complete the circuit, a sufficiently large current should flow so that in a few minutes the brass strip will be coated with gray zinc, and enough chlorine will be evolved to be seen in the cylinder.

#### 4. The Present-day View of Electricity.

Before considering, in detail, the changes in the preceding, it will be profitable to learn how electricity is now pictured in the minds of men who know something about it. It is thought to be something like a very light gas composed of particles called *electrons*. All substances contain these electrons—they are a component of all matter. Even substances which appear to us to be electrically neutral contain *electrons;* they do not appear to be "electrically charged" even though they contain electrons, because in all electrically neutral substances the "electron-pressure" is the same and hence electrons do not pass from one to the other,—just as bodies which are at the same temperature do not warm or cool each other—i. e., they do not transfer heat from one to the other.

When substances contain more electrons than they contain in the "neutral" state, they are said to be charged *negatively*. When "neutral" substances have lost one or more of their electrons, they are said to be charged positively.

Monovalent anions—such as the chloride ion ($Cl^-$), the nitrate ion ($NO_3^-$), the hydroxyl ion ($OH^-$)—are considered to be compounds of material atoms denoted by the symbols plus one electron more than they have in their neutral state. Bivalent anions—such as ($O^{--}$), ($SO_4^{--}$)—are compounds of the material atoms plus two electrons, etc. Monovalent cations—such as $Ag^+$, $Na^+$, $K^+$, $H^+$—are atoms of the respective elements which have given up one of the electrons which they contained as neutral substances. Bivalent cations, such as $Cu^{++}$, $Pb^{++}$, $Ca^{++}$, have given up two electrons, etc.

What is commonly denoted by *"the* electric current flowing through a circuit" is the flow of positive charges which have heretofore been assumed to exist: this direction of flow is one decided upon *by* convention. Instead of this flow of positive charges, we now consider the electrons (negative charges) as flowing in the opposite direction. Algebraically, these two expressions amount to the same thing, because a negative quantity moved in a negative direction is equal to the same quantity with a positive sign and moved in a positive direction. Hence, throughout the consideration in this book, we shall consider *only* the direction of the flow of negative charges or electrons, and we shall always speak of it as *"the direction of the electron flow."* Electrons by themselves are designated by a minus sign placed within brackets; e. g., (—)

**5. Consideration of Changes That Have Taken Place in the Electrolysis of Zinc Chloride.**

We shall now consider the changes that have taken place in the electrolysis of zinc chloride. The *facts* that were observed by the student were the changes that took place at the poles of the electrolytic cell: (1) at the negative pole (brass pole) grey metallic zinc was deposited, and (2) at the positive pole (carbon pole) chlorine gas was evolved. The following discussion will seek to present the explanation of the *observed* phenomena from the viewpoint of generally accepted theory. At the *brass* pole, negative electricity (electrons) were forced into the sheet brass and entered the layer of solution next to it. These electrons reacted (or combined) there with the only substances present with which they could react—the $Zn^{++}$ ions—according to the equation

$$Zn^{++} + 2(-) = Zn^{\circ}$$

Simultaneously with this action the opposite kind of a reaction was going on at the carbon pole. The action of the battery cell or dynamo (think of it as an electric pump) draws electrons out of this region, causing the chlorine ions next to the carbon pole to give up their electrons and change to the neutral form or gaseous chlorine. The reaction that takes place is

$$2Cl^{-} - 2(-) = Cl_2^{\circ}$$

It should be noted that there were withdrawn from the carbon pole as many electrons as were sent into the brass pole; the battery cell or dynamo, *in effect,* has merely served "to pump" these from the carbon pole to the brass pole.

**6. The Unseen Third Action of the Cell; The Transport of Ions.**

The discharge of cations at the cathode leaves the portions of the solution from which they are taken momentarily with more

anions than correspond to the cations present. At the anode the discharge of anions leaves these portions of the solution momentarily with more cations than correspond to the anions present. On account of their electric charges, these unbalanced anions at the cathode tend to draw together *with cations in adjacent drops of liquid,* and both move until they are in the "same drop" of liquid; i. e., until they have formed "neutral" drops,—drops which contain an equal number of positive and negative charges: the anions thus displaced in these adjacent drops do the same with the cations in the drops still farther on, etc. At the same time the cations which remain unbalanced at the anode tend to draw together with the anions in drops adjacent to them. These two tendencies assist each other, and, extending from cathode to anode, they bring about a slight shift of all the cations towards the cathode and of all the anions towards the anode. These shifts move the ends "of these lines farther from the poles": thus the solutions next to the poles become more dilute. Since some kinds of ions move more easily than other kinds, the mutual attraction moves the one kind of ions faster than the other kind, and hence the impoverishing of the solution may be more rapid at one pole than at the other.

To illustrate this effect by means of a model, draw with the aid of a small coin or a compass a row of contiguous circles, of about ¾ inch diameter, entirely across the upper edge of a sheet of writing paper 8 or 9 inches in width. The sides of the sheet are to represent the poles, and these circles a row of adjacent drops extending from cathode to anode. Put in each upper half of the circles a plus sign, and in each lower half a minus sign to represent an equal number of positive and negative charges in each drop. Cut the strip of circles from the sheet, and split it into two strips by cutting along the line of centers of the circles. Lay the strips side by side on the rest of the sheet with the ends of the strips coinciding with the sides of the sheet underneath.

To represent the discharge of a positive ion, fold the left end of the upper strip so as to place the first half circle underneath this strip; do the same with the last half circle on the right end of the lower strip. Next move the upper strip ¾ of the diameter of the circles to the left, and the lower ¼ of the diameter to the right, and note that the left circles in the two strips meet each other again. Note that the left ends of both detached strips are only ¼ diameter from the left-hand edge of the original sheet on which they rest, while the right ends are ¾ diameter from the right-hand edge of the original sheet. This indicates that there is a loss of dissolved substance at both poles and that the loss of dissolved substance on the right is three times as great as on the left.

### 7. Effect of Prevention of Transport of Ions.

One more question needs to be considered: would these changes take place if the two poles were placed in separate beakers so that the liquid would not extend from one pole to the other? The answer is: strictly speaking, these actions will take place at first, but will cease before *appreciable* amounts of ions are discharged, because the excess of anions remaining in the beaker in which cations are discharged, charge this region electrically negative, and the excess of cations remaining in the beaker in which the anions are discharged charge that region positively, and these electric pressures act *counter* to the electro-motive force which impels the current; hence the current will flow only until this "back pressure" in the beakers is equal to the applied electromotive force.

### 8. The Electrolysis of Hydrochloric Acid.

**Experiment.**—Secure a 1-liter beaker full of dilute hydrochloric acid and dip into it the carbon poles used in the preceding experiment, and dip into it also a hydrogen pole prepared as follows: a glass tube similar to the one used to make the carbon pole in the preceding experiment is fitted with a two-hole rubber stopper. One hole should be such as to admit a stout lead wire (diameter $\frac{1}{8}$ inch or more), which should extend almost to the other end of the tube and be bent into the form of a spiral near its free end. Into the second hole of the rubber stopper should be fitted a piece of narrow glass tubing, about 24 inches and bent so as to extend from the inner surface of the rubber stopper into the water in a vessel standing beside this electrolytic apparatus: by means of this tube, hydrogen is to be collected in a bottle inverted over water. Connect the carbon rod to the positive pole of the source of direct current, and the lead pole to the negative pole, and apply such an electromotive force that a bottle full of hydrogen may be obtained in a short while (10 minutes). Test the hydrogen by igniting it.

In this case, hydrogen ions are the only substances present which can combine with the electrons. They react at the cathode according to the equation—

$$2H^+ + 2(-) = H_2°.$$

At the other pole, where the electrons are "drawn out of the solution," the chlorine ions again give up electrons. It appears from a comparison of this experiment with the preceding that the action of the liberation of chlorine takes place irrespective of the *kind* of an action taking place at the other pole.

### 9. The Electrolysis of Dilute Sulphuric Acid.

**Experiment.**—Prepare another "lead pole" just like the cathode in the preceding experiment, and dip this and the cathode from the preceding experiment into a 1-liter beaker full of dilute sulphuric acid. Attach the connecting wires to sources of direct electric current, and apply a suitable electromotive force to obtain a fairly rapid evolution of the

gases at the poles. Collect the hydrogen and oxygen obtained in 100 c.c. cylinders and note, roughly, their relative rates of evolution.

At the negative pole, hydrogen is evolved as in the preceding experiment, but at the positive pole, oxygen is obtained. Identify these gases by any suitable means.

In order to understand this liberation of oxygen at the positive pole, we must realize (1) that water is undoubtedly ionized partly into $H^+$ and $O^{--}$ ions; and (2) that the discharge of $O^{--}$ ions would be just as much the action of the positive pole (anode!) as the discharge of $SO_4^{--}$. Since nothing but oxygen is obtained, we conclude that the oxygen ions from water are more easily discharged than the $SO_4^{--}$ ions; hence the action at this pole is represented by the equation—

$$2O^{--} - 4(-) = O_2^{\circ}$$

or $$2O^{--} = O_2^{\circ} + 4(-)$$

### 10. The Electrolysis of $Na_2SO_4$ Solution.

**Experiment.**—Secure a 1-liter beaker full of a *concentrated* sodium sulphate solution; dip into it the two "lead poles" used in the electrolysis of dilute sulphuric acid. Apply a fairly high electromotive force so that a fairly large current will flow in spite of the relatively poor conductivity of the salt solution. Oxygen and hydrogen will be obtained as with dilute sulphuric acid.

In this solution we have, for cations, both $H^+$ and $Na^+$ ions, and the cathode action apparently might take place with either one of these; the fact that hydrogen gas is obtained indicates that hydrogen ions are more easily discharged; and hence the pole action is represented by the equation—

$$2H^+ + 2(-) = H_2^{\circ}.$$

The action at the anode is the same as in the preceding experiment.

Dip strips of blue and red litmus paper into each one of the cups and also test some of the original electrolyte:—the liquid around the cathode will turn litmus blue and that around the anode will turn litmus red. These effects are due to the presence of $OH^-$ and $H^+$ ions, respectively.

Both of these ions are the remaining parts of the molecules of water of which the $H^+$ and $O^{--}$ ions, respectively, has been discharged.

### 11. The Electrolysis of Copper Sulphate Solution.

**Experiment.**—Secure a 1-liter beaker full of a moderately concentrated solution of copper sulphate (a 10 per cent solution). Put into it—suspended from the edge—a strip of sheet brass about 2x8 inches and connect it to the cathode. Dip into the solution the "lead anode" from the preceding experiment; electrolyze the solution with a moderately large current, but avoid a current so large as to form a "spongy" copper deposit. Note the copper deposited, and identify the gas obtained at the anode. Write the equation for both pole actions.

### 12. The Electrolysis of a Solution of Sodium Chloride.

**Experiment.**—Secure a 1-liter beaker full of a fairly concentrated sodium chloride solution (20 per cent), dip into it the "carbon anode" from Exp., Art. 3, and the lead cathode from the preceding experiment. Turn on the current, identify the products, and write the equations for the pole actions.

### 13. The Complete Independence, from Each Other, of the Actions in an Electrolytic Cell.

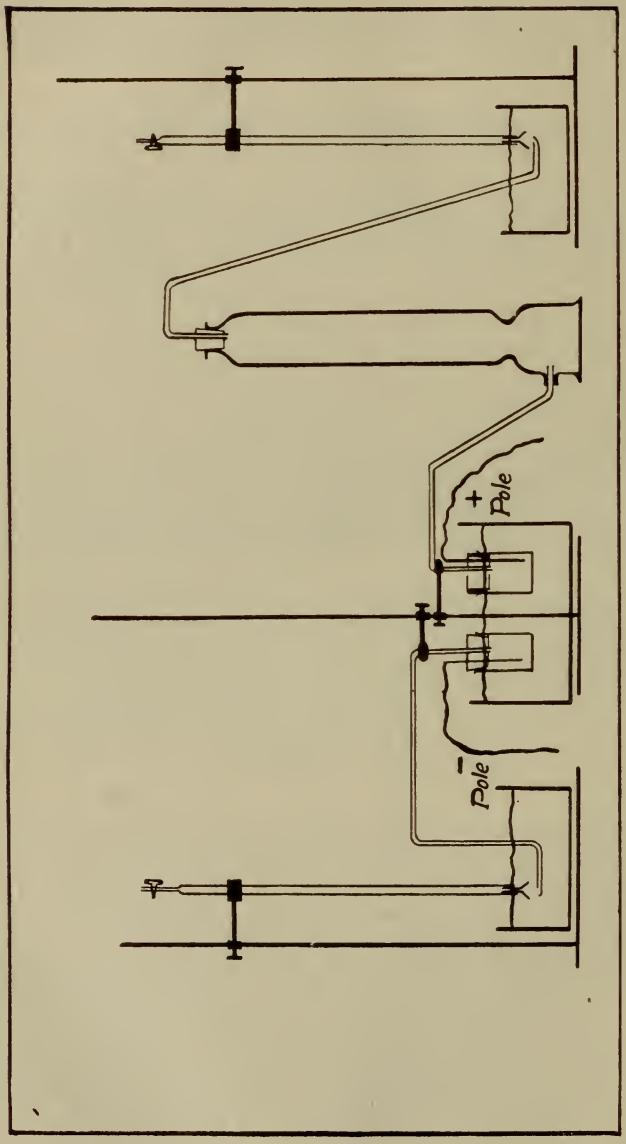
The fact that both in hydrochloric acid and in dilute sulphuric acid, the same cathodic action—i. e., the discharge of hydrogen ions—took place, although the anode actions were different, and, again, the fact that both in zinc chloride solution and in hydrochloric acid, the same anode action—i. e., the discharge of chlorine ions—took place, although the cathode actions were different, these and other such illustrations obtained from the above experiments show that the nature or kind of a change taking place at one pole of an electrolytic cell is independent of the nature or kind of a change taking place simultaneously at the other pole.

Furthermore, it is plain from the explanation in Art. 6 that the *third* action in every cell—i. e., the electric transport of ions—does not move *certain* ions, but moves any ions which are present. Thus in the electrolysis of sodium sulphate solution, the ions present in largest amount, and hence mostly available for this electric transport or "third action of the cell" are $Na^+$ and $SO_4^{--}$ ions, and these are the ions which take part in this third action of the cell, though neither one of them takes part in the other two actions—the discharge at the poles.

From all this it is evident that the three changes in an electrolytic cell are distinct and independent of each other. This is shown very strikingly by the arrangement in the following experiment:

### 14. To Demonstrate the Quantitative Relation Between the Hydrogen and Chlorine Evolved Simultaneously by Electrolysis.

**Experiment.**—Secure two small porous earthenware cups, 3 to 4 inches in height and $1\frac{1}{2}$ to 2 inches in diameter. Dip their upper edges in melted paraffin to a depth of one inch in order to close up the pores in these parts of the cups. Secure two rubber stoppers large enough to fit these cups. Perforate one with two holes so as to admit a small graphite rod, and a narrow piece of glass tubing; perforate the other two with holes so as to admit a stout lead wire, and also a piece of narrow glass tubing. Secure three glass jars or beakers, two of which are to be filled with water and are to be used to collect gases—in burettes, over water—as shown in the accompanying sketch. The third is to be filled with a saturated solution of salt—sodium chloride—and into this are to be placed the porous cups. Secure the rest of the apparatus and connect it as shown in the accompanying sketch. Note that the ends of the conducting tubes under the burettes are drawn out to fine openings, bent so as to be horizontal, and placed as high in the water as possible.




Demonstration of Ratio of Hydrogen to Chlorine Produced Electrolytically.

Fill the negative pole cup—the one with the lead wire—about half full of dilute sulphuric acid. Fill the other pole half full of a mixture prepared as follows: Dilute one part of concentrated hydrochloric acid with one part of water, and add a little chloride of lime:—enough chlorine should be evolved by the action of this mixture to saturate the liquid.

Connect up the whole apparatus, turn on a moderate current, and allow it to run for a few minutes until it appears that the gases collect in the burettes at equal rates. Then interrupt the electric current, refill the burettes with water, and turn on the electric current again. Note the rates at which the gases collect in the burettes. Repeat the measurement. How is the ratio of these volumes of hydrogen and chlorine, respectively, related to the ratio in which the gases combine by volume?

Note, however, that in this electrolytic cell, the hydrogen is evolved from sulphuric acid, the chlorine from hydrochloric acid, and the ions transported between the poles are those of sodium chloride. The result would have been the same had hydrochloric acid been used in all compartments of the cell, but this arrangement serves incidentally to point out the independence of the three actions in a striking way.

## CHAPTER XII.

## BATTERY CELLS AND OXIDATION-REDUCTION REACTIONS.

### 1. The Products of Electrolysis Are Electromotively Active Substances.

If an electrolytic cell has had a current passing through it for a while, and then the wires connected to its poles are disconnected from the source of electric current and connected with their loose ends to a voltmeter, the needle of the latter will deflect so as to indicate that a current is flowing in the direction opposite to that of the previous electrolyzing current. As this current is allowed to flow, the electrolytic products present at the poles change back to the original substances which they were before electrolysis had begun,—or, in other words, the pole reactions take place in a direction the reverse of that in which they took place during electrolysis.

**Experiment.**—Secure the apparatus used in Experiment, Chapter XI, Article 3, and connect a voltmeter (range, about 3 volts) to the poles of this cell before any current has been sent through it. The voltmeter should show practically no deflection, but if it shows any deflection, its poles should be "short-circuited" a few minutes by connecting them directly with a copper wire. When the voltmeter is applied again, practically no deflection will be observed. This shows that there are no substances in the cell which tend to produce a continuous current.

Now connect the cell to the source of a direct electric current, and allow enough current to pass to deposit an appreciable amount of zinc, and evolve a noticeable amount of chlorine. Then apply the voltmeter again: it should register about 2 volts.

The deflection of the voltmeter indicates that electrons are flowing through the wire and voltmeter *from* the zinc electrode to the chlorine electrode—i. e., in a direction opposite to that in which they flowed when zinc and chlorine were formed by electrolysis. With this new direction of flow of electrons,—the zinc and chlorine change back to zinc ions and chloride ions, respectively—i. e., the pole reactions now take place in a sense expressed as follows:

$$Zn^\circ \longrightarrow Zn^{++} + 2(-)$$
$$Cl_2^\circ + 2(-) \longrightarrow 2Cl^-.$$

Since no other force is acting in this circuit, it is evident that these substances must exert a tendency to change back to zinc ions and chloride ions, respectively, or at least, one of them must exert such a tendency with sufficient force to overcome any opposing tendency of the other. The latter is the simplest view to take. According to this view, in a disconnected battery pole, the materials react until the electrons produced exert a sufficient

pressure to stop further change. Then when the two poles in a cell are connected the flow of electrons through the connecting wire will take place just like the flow of a gas through a pipe; that is, from the pole in which the electrons are under greater pressure to the pole in which they are under lesser pressure. Evidently, in the cell under consideration, the zinc pole is the one in which the pressure or concentration of electrons produced by the reaction

$$Zn^{\circ} = Zn^{++} + 2(-)$$

is greater than the pressure or concentration of electrons in the chlorine pole produced by the reaction

$$2Cl^{-} = Cl_2^{\circ} + 2(-)$$

As the electrons flow out of the zinc pole, zinc changes to zinc ions to replace the electrons which have flown out; and as the electrons flow into the chlorine electrode, chlorine changes to chloride ions to use up the electrons which have arrived. Furthermore, the electromotive force or voltage between the poles is directly dependent upon the difference between the electron pressures or concentrations in the two poles, and hence serves as a measure of this difference between the electron pressures.

### 2. The Electromotive Tendency Possessed by Some Substances is Their Natural Property, and Does Not Depend on Their Methods of Preparation.

In order to obtain a cell which tends to send out an electric current, we need merely to secure a cell arranged for electrolysis and place, in contact with their respective poles, some of each of the two materials that would be produced by electrolysis at the two poles; however, these materials need not have been obtained by electrolysis, but may have been prepared by any chemical process whatever. Thus, whenever zinc and chlorine from any sources whatever are placed in a cell arranged for the electrolysis of zinc chloride, the cell will always act to produce an electric current with the same voltage. This will be shown in the experiment below. Such an arrangement of material which tends to send out an electric current is called a *battery cell.*

### 3. The Poles of Battery Cells Are Independent of Each Other in Their Behavior.

**Experiment.**—(a) Secure five small porous "battery" cups, and fill them as follows:

1. Fill with a solution of zinc sulphate and put in a rod of zinc or a clean strip of sheet zinc with a "wire connector."
2. Fill with a solution of cadmium sulphate, and put in a rod or strip of sheet cadmium with a wire connector.
3. Fill with a solution of copper sulphate and insert a bright piece of sheet copper with a wire connector.

4. Fill with dilute hydrochloric acid to which has been added 2 or 3 grams of bleaching powder—i. e., enough to saturate the solution with chlorine. Insert an electric arc carbon or a graphite rod with a copper connecting wire well "twisted" on.

5. Fill with a solution of iodine in potassium iodide, and insert a carbon rod as in No. 4.

Secure a large beaker half filled with saturated sodium chloride solution. Put the zinc pole cup into this beaker, and connect the zinc to the negative connector on a voltmeter (with a range of 3 volts or only slightly more).

Then insert, in turn, cups 2-5, connecting the poles, in turn, to the positive connector of the voltmeter. The voltages measured should be approximately as follows:

Cadmium against zinc, 0.36 volt.
Copper against zinc, 1.10 volts.
Iodine against zinc, 1.30 volts.
Chlorine against zinc, 2.11 volts.

Now let us consider the zinc pole to be a "common reference pole," and tabulate the voltages of all the cells formed by combining these poles in turn with this "reference pole." The voltage of the cell formed by combining the zinc pole with itself will naturally be zero; and the others give the values obtained above. Thus the following table will be obtained:

| | Volts against zinc | Volts against (zinc —2.76) |
|---|---|---|
| Zinc pole | 0.0 | —2.76 |
| Cadmium pole | 0.36 | —2.40 |
| Copper pole | 1.10 | —1.66 |
| Iodine pole | 1.30 | —1.46 |
| Chlorine pole | 2.11 | —0.65 |

Finally, let us subtract 2.76 from each value and thus obtain the voltages of cells formed by combining these poles, in turn, with a pole which combined with the zinc pole would give a cell with a voltage of 2.76 volts (with the zinc as the negative pole). These values are given in the last column of the table above. They are the same as the values in the large table below, and this illustrates how the voltages in the large table were obtained.

If, in their behavior, the poles of battery cells are independent of each other, then the electric pressure set up in each one by the reacting substance in it is always the same; and the voltages in the above table which show or "measure" the differences between the electron pressure of the zinc pole and the other poles above, should give us, by simple subtraction, the voltage between any other combination of these poles. This will now be shown to be true.

**Experiment.**—(b) The table shows that the voltage of the cell composed of a copper pole and a chlorine pole should be 1.0 volt, with the copper as the negative pole; that of the cell composed of the copper and

of the cadmium pole should be 0.74 volt with cadmium as the negative pole. Verify these experimentally with the apparatus in the experiment above. What changes take place during action in the copper-chlorine cell? What changes in the copper-cadmium cell? Try the other combinations possible and state how the pole materials change in them.

#### 4. The "Third Action" in Every Battery Cell.

The two poles of a battery cell must be connected by a salt solution for the same reason for which the poles of an electrolytic cell must be thus connected:—while the cell is sending a current through the wire from one pole to another, the reaction taking place at one pole will result in the temporary presence of an *excess of cations* over anions in that region, and the action at the other pole will result in an excess of anions over the cations in the latter region, and these two excesses are equalized by the double shift of ions throughout the solutions extending from pole to pole, as was pointed out in the study of electrolytic cells.

#### 5. A Table of Electromotive Reactions.

By means of the same procedure as that employed with the five poles in the table above, all the common electromotively active substances have been tabulated, and thus the following table was obtained. The voltages given correspond to the electromotive forces of the cells that would be formed by combining the pole made from each substance, in turn, with the same positive pole. The latter has such an electron pressure that a cell formed by combining it with a zinc pole would have an e.m.f. of 2.76 volts; or combined with an acid-hydrogen pole (No. 17), an e.m.f. of 2 volts.

The substances in the *left* column tend to change to the corresponding substances in the *right* column with forces proportional to the numbers in the central column. The minus signs in front of these numbers may be ignored:—they are added merely to indicate that these poles act as *negative* poles when combined with the common reference pole to form battery cells.

TABLE OF ELECTROMOTIVE REACTIONS ARRANGED IN DESCENDING ORDER OF THE ELECTRIC PRESSURES PRODUCED THROUGH THEIR REACTION TENDENCIES.

| Elements in Reduced State (in Order of Decreasing Powers of Acting as Reducing Agents). | Relation of Tendency to Change From Left to Right, Expressed in Volts. | Elements in Oxidized State (in Order of Increasing Powers of Acting as Oxidizing Agents, see Note 1 below). |
|---|---|---|
| 1 Potassium metal (See Note 2) | —5.00 | $K^+$ Salt solution +1 (—) |
| 2 Sodium metal | —4.80 | $Na^+$ Salt solution +1 (—) |
| 3 Calcium metal | —4.50 | $Ca^{++}$ Salt solution +2 (—) |
| 4 Magnesium metal | —3.50 | $Mg^{++}$ Salt solution +2 (—) |
| 5 Aluminium metal | —3.00 | $Al^{+++}$ Salt solution +3 (—) |
| 6 Hydrogen gas (See Note 3) | —2.80 | $H^+$ ions in NaOH sol. (normal in $OH^-$) +1 (—) |
| 7 Zinc metal | —2.76 | $Zn^{++}$ Salt solution +2 (—) |
| 8 Sulphide ion (Sodium sulphide solution normal in $S^-$) | —2.55 | S° element +2 (—) (See Note 3) |
| 9 Iron metal | —2.43 | $Fe^{++}$ Salt solution +2 (—) |
| 10 Cadmium metal | —2.40 | $Cd^{++}$ Salt solution +2 (—) |
| 11 Sulphide ion (Sat. sol. of hydrogen sulphide in pure water) | —2.35 | S° element +2 (—) (See Note 3) |
| 12 Lead metal (See Note 4) | —2.34 | $Pb^{++}$ in dil. $H_2SO_4$ +2 (—) (Sat. sol. of $PbSO_4$) |
| 13 Nickel metal | —2.17 | $Ni^{++}$ Salt solution +2 (—) |
| 14 Sulphide ion (Sat. sol. of $H_2S$ in normal HCl) | —2.15 | S° element +2 (—) |
| 15 Lead metal | —2.12 | $Pb^{++}$ Salt solution +2 (—) (normal in $Pb^{++}$; see also No. 12 above and Note 3) |
| 16 Tin metal | —2.10 | $Sn^{++}$ Salt solution +2 (—) |
| 17 Hydrogen gas (See Note 3) | —2.0 | $H^+$ ions in acids +1 (—) (normal solution of $H^+$ ion) |
| 18 Bismuth metal (same for Sb) | —1.8 (?) | $Bi^{+++}$ Salt solution +3 (—) |
| 19 Stannous ion (stannous chloride solution) | —1.76 | $Sn^{++++}$ Salt solution +2 (—) (stannic chloride sol.) |
| 20 Mercury metal | —1.70 | $Hg^+$ Salt solution +1 (—) ($Hg_2Cl_2$ in normal $Cl^-$ sol.) |
| 21 Copper metal | —1.66 | $Cu^{++}$ Salt solution +2 (—) |
| 22 Iodide ion (normal in $I^-$) | —1.46 | I° element +1 (—) (Sat. sol. of iodine) |
| 23 Ferrous ion (Sol. normal in $Fe^{++}$) | —1.25 | $Fe^{+++}$ Salt solution +1 (—) (normal in $Fe^{+++}$) |
| 24 Silver metal | +1.20 | $Ag^+$ Salt solution +1 (—) |
| 25 Mercury metal | —1.14 | $Hg^+$ Salt solution +1 (—) |
| 26 Oxygen ion (in NaOH Sol. normal in $OH^-$ ions) | —1.12 | Oxygen gas (sat. sol.) +2 (—) |
| 27 Bromide ion (sol. normal in $Br^-$) | —0.92 | Br° element (sat. sol) +1 (—) |
| 28 Sulfur in compounds, with valence less than 6 (+) (See Art. 22) | —0.80(?) | $S^{6+}$ compounds + free (—) (conc. $H_2SO_4$) |
| 29 Chloride ion (sol. normal in $Cl^-$) | —0.65 | Cl° element (sat. sol.) +1 (—) |
| 30 $Cr^{+++}$ compounds (See Note 5) | −0.7 to −0.50 | $Cr^{6+}$ compounds + free (—) (Sol. of chromic acid) |
| 31 $Mn^{++}$ compounds (See Note 6) | —0.49 (?) | $Mn^{7+}$ compounds +5 (—) (Sol. of permanganate) |
| 32 Nitrogen in compounds, with valence less than 5 (+) (See Art. 14) | −0.80 to −0.30 | $N^{5+}$ compounds ($HNO_3$) +free (—) |
| 33 Cl° element (See Art. 25) | ? | Chlorine in compounds where it has positive valence + free (—) (NaOCl, $KClO_3$) |
| 34 Oxygen ions (in any acid sol. having very few $O^{--}$ ions) | —0.30 (?) | Oxygen gas liberated from a platinum pole by electrolysis of sols. of oxy-acids such as nitrates, sulphates, phosphates + free (—) |
| 35 $Pb^{++}$ ion (in sat. sol. of $PbSO_4$ in dil. $H_2SO_4$ (See Note 7) | —0.34 | $Pb^{4+}$ (from $PbO_2$—solid in dil. $H_2SO_4$) + free (—) |
| 36 Fluoride ion sol. (See Note 8) | —0.10 | F° element + 1 (—) |
| 37 Theoretical zero pole | 0.00 | Theoretical zero pole |

### 6. Notes on the Table of Electromotive Reactions.

NOTE 1.—The voltages in this table have been obtained by using poles in which all solutions have *normal* concentrations of the ingredients mentioned except where other concentrations are stated specially in the table. Since the reacting tendencies of substances vary with their concentrations, it follows that the tendencies to reaction will be different when the concentrations of the substances are different from those given here:—the voltages in the central column will be *larger* if the substances in the *left* column are employed in a *more concentrated form* than that here mentioned,—the voltages will be *less* if the substances on the *right* are present in a more concentrated form than that here mentioned.

NOTE 2.—Metals Nos. 1-5 in left column react on contact with water ($2K+2HOH=2KOH+H_2$), and hence can be used to react with other substances only when water is absent.

NOTE 3.—The relative tendencies to reaction indicated by the position of these substances in the table is not changed extensively by *ordinary* diluting or concentrating of the solutions; but with large differences in concentrations, such as the difference between the hydrogen ion concentration in an acid on one hand and in pure water on the other (the latter contains one-ten millionth as much H ion as the former!), the voltage of the same material has largely different values. Only on this account do some materials appear at several different places in the table. Compare No. 6 with No. 17 and No. 8 with 11 and 14.

NOTE 4.—See Note 3 and compare No. 12 with 15.

NOTE 5.—The reaction for the change of bichromates in No. 30 is—

$$7H_2O+2K^+ +2Cr^{+++} \leftarrow K_2Cr_2O_7+6(-)+14H^+$$

NOTE 6.—The equation for No. 31 is—

$$4H_2O+K^+ +Mn^{++} \leftarrow KMnO_4+5(-)+8H^+$$

NOTE 7.—The equation for the change in No. 35 is—

$$2H_2O+PbSO_4 \rightleftharpoons PbO_2+2(-)+4H^+ +SO_4^{--}$$

NOTE 8.—Fluorine gas reacts on contact with water—

$$(2F_2+2H_2O=2H_2F_2+O_2)$$

and hence can be used to react with other substances only when water is absent.

### 7. Exercise on the Table of Electromotive Reactions.

A. To select the materials for any battery cell possible with the common substances, proceed as follows: Select any substance

in the left-hand column for the negative pole—it will change to the corresponding substance in the *right-hand* column, if any substance in the right-hand column on a lower line is placed at the positive pole. The latter is forced to change to its corresponding substance in the left-hand column because the change of the first substance produces a greater electron pressure than the second can withstand. The voltage of the cell is equal to the voltage of the first change minus the voltage of the second change.

1. The well known Daniell cell is made up by placing zinc (i. e., No. 7 *left*) at the negative pole, and copper sulphate (i. e., No. 21 *right*) at the positive pole. Its voltage is 2.76—1.66 =1.10 volts. Its pole reactions are:—

$$Zn^{\circ} = Zn^{++} + 2(-)$$

$$Cu^{++} + 2(-) = Cu^{\circ}$$

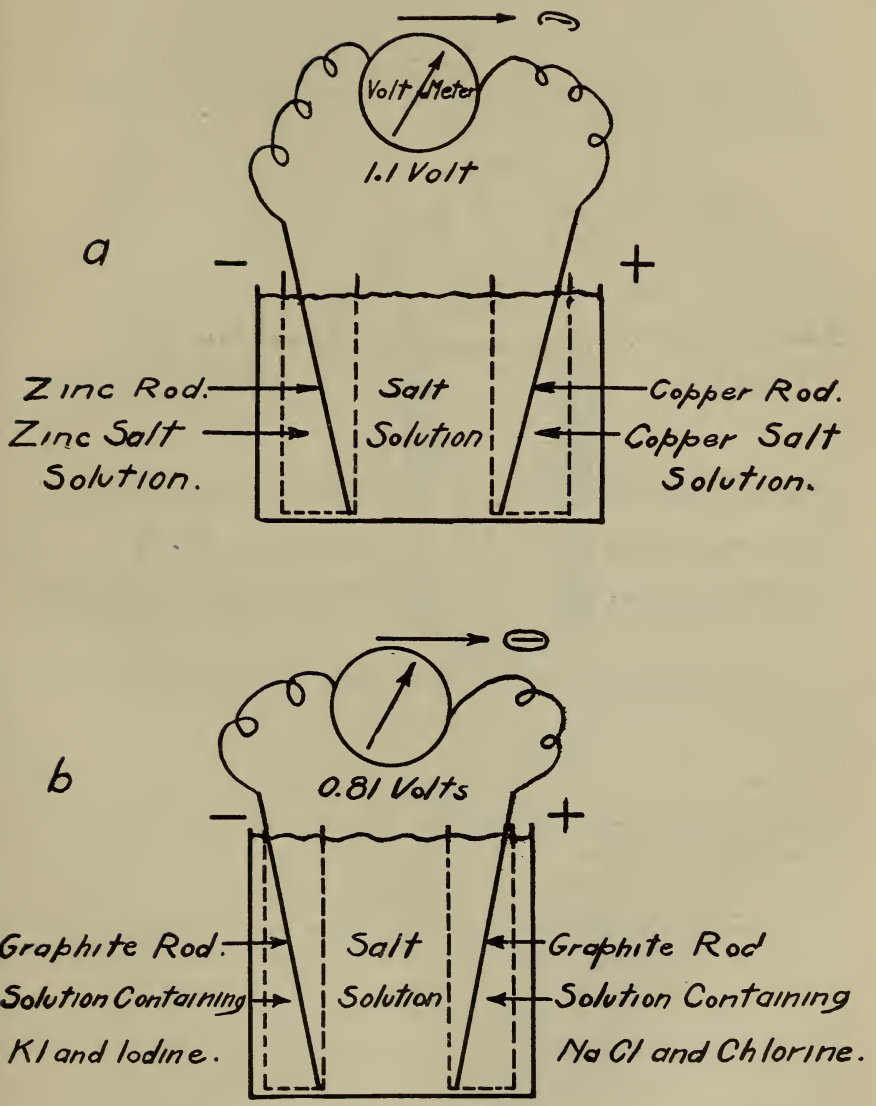
Make a list of other cells in which the same kind of change take place—of a free metal at the negative pole and of a metal ion at the positive pole. State their voltages and write their pole reactions.

2. Write the pole reactions of a cell composed of No. 21 *left* and No. 29 *right*. What is the voltage of this cell? Make a list of other cells in which the same kind of changes take place—of an anion at the negative pole and of a free non-metal at the positive pole. State their voltages and write their pole equations.

3. Write the equation for No. 19 changing from the substance on the left to the substance on the right. Ditto for No. 23. Combine No. 19 *right*, and No. 23 *right*, each in turn, with No. 7 *left*. State the voltages of the combinations and write the pole equations.

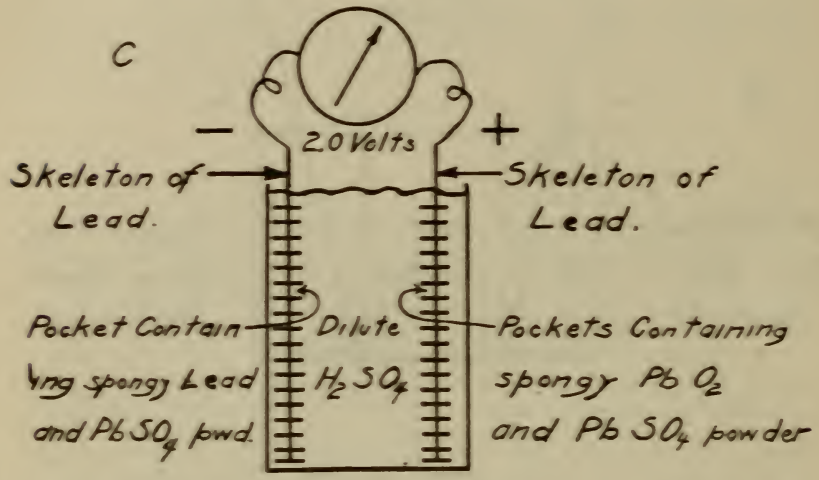
B. For the actual construction of battery cells, we must secure in general, a jar or beaker filled with a concentrated salt solution, and put into it two porous earthenware cups as in Experiment, Art. 3. Put into one cup *all* the materials named in both right and left columns of one of the horizontal lines selected for this cell from the table, and put into the other cup *all* the materials named in the other line. The metallic materials must be supplied in a shape which admits of connecting them to the conducting wire; in the absence of a metallic material in the pole, a rod of a chemically inactive material must be supplied to make the electrical connection (in general, a rod of graphite!). These changes and the electromotive forces will be exactly as inferred from the data in the table. An "outline" sketch of the cross-section of the battery cell thus assembled is shown in the accompanying figures—(a) from lines 7 and 21, and (b) from lines 22 and 27.

1. Make sketches similar to (a) of the battery cells obtained with 10 and 24, 15 and 21, 7 and 15.


Volt Meter
1.1 Volt
a
−
+
Zinc Rod.
Zinc Salt Solution.
Salt Solution
Copper Rod.
Copper Salt Solution.
0.81 Volts
b
Graphite Rod.
Solution Containing KI and Iodine.
Salt Solution
Graphite Rod
Solution Containing Na Cl and Chlorine.

2. Make sketches similar to (b) of the battery cells obtained with lines 22 and 27, 8 and 22, 27 and 29.

3. Figure (c) is a diagram of the essential parts of the lead storage battery, which is built up from the materials mentioned in lines 13 and 35. Note that the poles contain all the materials mentioned in these lines,—that the liquid around both poles is the same, hence there is no need of porous cups nor of another connecting solution. (See footnote.)




The reactions of the "valence-changers" in the poles of the storage battery are:

$$Pb^{++} = Pb^{++} + 2(-)$$

and $$Pb^{++} + 2(-) = Pb^{++}$$

Both of these reactions are immediately followed by the combining of the $Pb^{++}$ with $SO_4^{--}$ ions. Hence the complete change at the negative pole is—

$$Pb^{++} + SO_4^{--} = PbSO_4 + 2(-)$$

At the positive pole, the reaction is further accompanied by the reaction of the $2O^{--}$ ions from the $PbO_2$ combining with $4H^+$ ions—

$$2O^{--} + 4H^+ = 2H_2O$$

Hence the complete change at the positive pole is—

$$PbO_2 + 4H^+ + SO_4^{--} + 2(-) = PbSO_4 + 2H_2O$$

FOOTNOTE.—The storage cell called "chloride accumulator" is so named because in its manufacture the "pockets" in the lead skeleton were first filled with melted lead chloride; and by electrolysis this material was then changed to spongy lead and lead peroxide, respectively.

C. It is shown at the opening of this chapter that the electrolysis of a solution of zinc chloride produced a battery cell with an electromotive force equal to the combined electromotive force of its products: zinc and chlorine. In order that the electrolyzing current may continue to flow, it must be impelled *from without* by a voltage or electromotive force *larger* than the opposing voltage of its products: *zinc and chlorine.* This opposing voltage or electromotive force of the products is called the *back or counter electromotive force,* and the value of this force in different examples may be ascertained from the table, as follows: A solution of zinc chloride is a solution of both chloride ions and zinc ions, or the material found in *29 left and 7 right.* It is evident that 29 left can change to 29 right only if the electrons produced thereby will be taken away. This is done by an "electric pump" (i. e., a battery or dynamo), which, in this case, sends the electrons to the other pole, where 7 *right* is made to take up the electrons and change to 7 *left.* The "pump" must exert an e.m.f. *larger* than the difference between that in 7 and 29.

1. Ascertain from the table, the back electromotive force which must be overcome by the applied e.m.f. when dilute hydrochloric acid is to be electrolyzed; when zinc iodide solution is to be electrolyzed; when cadmium bromide solution is to be electrolyzed.

2. Compare the voltage required to electrolyze HCl solution with that required to electrolyze HBr solution. If the solution in an electrolytic cell contained both of these substances, and the voltage applied at the poles began with a zero value and were increased gradually until a *continuous* current *first* begins to flow, which one of the two anions present would be discharged? If HI were also in the solution, which anion would be discharged with the least *e.m.f.* applied to the cell? In general, what is the relative position in the table of the first of several anodic changes possible that would take place?

3. Ascertain, from the table, the back electromotive force that must be overcome by the applied electromotive force when a solution of copper sulphate is to be electrolyzed. Compare this with the back electromotive force in the electrolysis of zinc sulphate solution. State which metal would be the first one to be deposited if a gradually increased voltage were applied to an electrolytic cell containing both of these salts. Which metal would thus be deposited first out of a solution of copper nitrate and silver nitrate? Which out of a solution containing cadmium chloride and mercuric chloride? In general, what is the relative position in the table of the first of several cathodic changes possible that would take place?

**8. Changes in Valence Correspond to a Change in the State of Oxidation of an Element.**

In its *primary* meaning, the term "oxidation" expresses the combination of a substance with oxygen. Thus the change of copper metal to copper oxide, CuO, is spoken of as oxidation of the copper. In its primary sense, reduction means simply the reverse of this change. But the term *oxidation* does not only include the changes in which oxygen *appears* as having combined with the substances said to be oxidized; it also includes such changes as the conversion of any free metal to any of its salts ($Cu^0$ to $CuCl_2$) and the liberation of a non-metal from its salts such as the liberation of chlorine from hydrochloric acid or from sodium chloride. The term oxidation has been extended so as to include these changes because when they are brought about in one way they certainly involve oxidation, and hence when they are brought about in any other way they are also considered as involving an equivalent change. Thus in the above example the $Cu^0$ may be oxidized first to CuO and then, by reaction with HCl, changed to $CuCl_2$, and since the latter change does *not undo* the first oxidation, the $Cu^{++}$ in $CuCl_2$ is still in the same state of oxidation as it was in CuO. Hence, whenever $Cu^0$ is changed to $CuCl_2$, the change *involves something equal to oxidation* and is spoken of as oxidation. Again, chlorine can be produced from hydrochloric acid *by reaction with free oxygen;* hence whenever a chloride is acted upon so as to produce free chlorine *by any means whatever*, the operation is considered to be equivalent to oxidation and is spoken of as such.

Thus it appears that all changes in valence correspond to changes in the *states* of oxidation of elements. More particularly, changes in valence which take place in the sense of—

$$\text{from } Cu^0 \text{ to } Cu^{++}$$
$$\text{or } Cl^- \text{ to } Cl_2^0$$

indicate *oxidation*. Both of these particular changes involve the giving up of electrons—

$$Cu^0 - 2(-) = Cu^{++}$$
$$2Cl^- - 2(-) = Cl_2^0$$

and hence the most general, and simple, definition for *oxidation* is this:—*oxidation is any change in which the valence of an element is changed in a sense which corresponds to the giving up of electrons.* Reduction is the reverse of such a change.

**9. Exercise.**

1. Of the *two* states of each element expressed here by symbols, which is the lower state of oxidation (or *reduced* state)?

a. Sulphur as $S^\circ$ or as $H_2S$?
b. Copper as $CuSO_4$ or as $Cu^\circ$?
c. Iodine as KI or as $I_2^\circ$?
d. Lead as $Pb^\circ$ or as $Pb(NO_3)_2$?
e. Lead as $PbSO_4$ or as $PbO_2$?

2. Judging from the data in the Table of Electromotive Reactions, have the elements in the following form any tendency to change to more oxidized states, or are they in the highest state of oxidation, and hence can be changed only by being *forced* back to more *reduced* states?

a. Copper in $CuSO_4$?
b. Chlorine in HCl?
c. Lead metal?
d. Iodine element?
e. Lead in $PbO_2$?
f. Sulphur in $H_2S$?
g. Cadmium in $CdCl_2$?
h. Chlorine gas?
i. Hydrogen gas?

**10. The Two Pole Actions of a Battery Cell Constitute an Oxidation-Reduction Reaction; and Vice Versa.**

**Experiment.**—(a) Put some finely granulated zinc, or some zinc "dust" into a test-tube, add some copper sulphate solution, and shake the mixture until the blue color of the copper ion (?) has disappeared. Note the color of the metal formed. Pour some of the resulting liquid through a filter and into another test-tube, add a little ammonia and $H_2S$ water. The formation of a white precipitate (ZnS) shows that zinc has been dissolved; i. e., changed to a salt.

The reaction in the mixture above is—

$$Zn^\circ + CuSO_4 = ZnSO_4 + Cu^\circ$$

$$\text{or } Zn^\circ + Cu^{++} = Zn^{++} + Cu^\circ$$

This reaction is evidently the sum of the two reactions—

$$Zn^\circ = Zn^{++} + 2(-)$$

$$Cu^{++} + 2(-) = Cu^\circ$$

which are the two pole actions that take place in the cell formed by coupling of the copper pole (No. 21) with the zinc pole (No. 7). This test-tube with zinc and copper solution contains *all* the parts necessary for the action of the cell, because in this cell only *zinc* and *copper ions* are changed. If we imagine the two poles and pole liquids in the preceding figure (a) brought together until the two porous cups become *one* and the poles touch, then no connecting wire is needed, the salt solution between the cups also is unnecessary, and the cup contains just the materials in the test-tube above; hence the test-tube above contains all necessary parts of the *whole cell,* and the same forces

which are active in the battery cell above must be the forces which bring about the reaction in the test-tube mixture.

There is no reason why we should assume that the materials in the test-tube react in a manner different from the manner in which they react in a battery cell,—which was represented as follows:—

$$Zn^{\cdot\cdot} = Zn^{\cdot\cdot} + 2(-)$$

and $Cu^{\cdot\cdot} + 2(-) = Cu^{\cdot}$

Since the *whole* reaction in the test-tube must be the *sum* of these two, we add the two left sides and the two right sides, and thus obtain:—

$$Zn^{\cdot} + Cu^{\cdot\cdot} + 2(-) = Zn^{\cdot\cdot} + Cu^{\cdot} + 2(-)$$

Allowing the electrons on the left to cancel those on the right, and adding the *combined* $SO_4^{\cdot\cdot}$ merely to give the formulæ of the *salts* instead of the formulæ of the free ions, we obtain the *common* form of the equation for this reaction in the test-tube mixture—

$$Zn^{\cdot} + CuSO_4 = ZnSO_4 + Cu^{\cdot}$$

In this action evidently zinc is oxidized and copper ion is reduced—the *amount of oxidation* being equal to the amount of reduction because zinc cannot change without getting rid of electrons and copper ion cannot change without receiving electrons. Hence the quantity of each substance which is changed depends upon the number of electrons transferred from the zinc to the copper ion, and this makes the amount of oxidation equal to the amount of reduction.

If cadmium metal is put into some copper sulphate solution, what reaction will take place? Of what two pole actions is it the sum? Which substance is oxidized, which reduced? Answer the same questions for a mixture of zinc and cadmium sulphate solution.

**Experiment.**—(1) Put some finely granulated or powdered zinc into a test-tube, add a little bromine water (or bromine solution), and shake the mixture until the color has disappeared. Test the solution for zinc ion as in the preceding experiment.

The action in this mixture is identical with the action in the cell formed of a zinc pole together with a bromine pole. Write the pole equation and add them up to obtain the equation for the reaction in this test-tube mixture. State what is oxidized, what reduced?

Recall (or try now) the reaction between potassium bromide (or iodide) solution and chlorine water. To what battery cell above does this mixture correspond? What is oxidized? What is reduced?

**11. The Reaction of Battery Cell Constituents.**

It is evident from these examples that the acting materials in any battery cell will react if mixed together,—hence any material in the left column of the Table of Electromotive Reactions will react with any material in the *right* column *below* the line of the first material. This includes all the oxidation-reduction reactions possible between the common substances.

In order to learn all the reactions possible, the student should learn the order of the substances in the left column, and the kind of substance each one changes into (given in the right-hand column, on the same line).

Then he should drill himself by answering the following questions, and make up and answer others like them. The substances in the upper part of the left column in the table should be remembered as being strong *reducing agents;* those in the lower part of the right column as strong oxidizing agents.

**12. Exercise.**

1. Judging from the information given in the table, will copper metal react with a solution of a mercuric salt? Put a bright strip of copper into a small amount of mercury salt solution, and note the result obtained. What is reduced? What oxidized? Write the equation from the reaction.
2. Recall the reaction between $SnCl_2$ and $HgCl_2$; in this change, which element is oxidized? Which reduced?
3. Ascertain from your text what metals are frequently found in the earth in the form of free metals,—which rarely,—and which are never found as free metals:—relate your findings to the order of the metals in this table.
4. What metals liberate hydrogen from acids? How must two metals be related in position in the table in order that one placed in a solution of a *simple* salt of the other will reduce the latter?
5. How must the non-metals—oxygen, sulphur, chlorine, bromine, iodine—be related in position in the table in order that one mixed with a solution of a "salt" of the other will oxidize the latter?
6. Will *11 left* (or *14 left*) react when mixed with *23 right?* What is oxidized? What is reduced? Figure out the equation for the reaction. Locate this equation in the preceding part of this manual.

**13. The Complete Ionization of Ternary Compounds, e. g., $HNO_3$, $H_2SO_4$, Etc., Into Ions Composed of Single Elements.**

The primary ionization of $NH_4Cl$ yields $NH_4^+$ and $Cl^-$, but complete ionization into the elemental parts requires the further ionization of $NH_4^+$. Since $4H^+$ result from this ionization, and

thus 3 new (+) charges appear. It follows that 3 (-) have been given up by the H's and these may be written as placed upon the N ion (written $N^{3-}$ or $N^{---}$). The whole compound in the form of ions appears as ($4H^{+}$, $N^{3-}$, $Cl^{-}$). In the same way the complete ionization of $H_2SO_4$ requires, after the primary ionization into $2H^{+}$ and $SO_4^{--}$, the further ionization of $SO_4^{--}$. Since $4O^{--}$ would result from this secondary ionization, and hence 6 *new* (-) charges appear, six electrons appear to have been obtained from the S, and hence this is written as having six (+) charges on it (written $S^{6+}$). Hence, sulphuric acid, completely ionized, appears as ($2H^{+}$, $S^{6+}$, $4O^{--}$).

It is not intended to convey the idea that these ternary substances separate extensively into their elemental ions before reaction takes place; it is merely intended to express the fact that they may do so: it is almost certain that *they undergo such ionization* gradually during the progress of an oxidation-reduction reaction.

Ascertain whether the italicized elements in the list below when changed from the first to the second compound undergo oxidation. Express the amount of change in numbers of electrons per atom of the changed element:

| | First Compound | Second Compound |
|---|---|---|
| (a) | $H_2S$ | $H_2SO_3$ |
| (b) | $HCl$ | $KClO_3$ |
| (c) | $H_2SO_4$ | $H_2SO_3$ |
| (d) | $HNO_3$ | $NH_4OH$ |
| (e) | $KMnO_4$ | $MnSO_4$ |
| (f) | $K_2Cr_2O_7$ | $CrCl_3$ |

### 14. Nitric Acid and Its Reduction Products.

The nitrogen in nitric acid and in nitrates is in the *highest* state of oxidation in which it occurs; and the nitrogen in ammonia or ammonium compounds is in the *lowest* state of oxidation,—it cannot be reduced further. Between these two limits there are a number of oxidation stages, the order and relation of which is shown in the following table. Note that the free element occupies an intermediate position.

TABLE OF NITROGEN COMPOUNDS IN THE ORDER OF THEIR EXTENT OF REDUCTION FROM NITRIC ACID.

| Compounds. | Elemental Ions from Theoretical Ionization. | Amount of Reduction from $HNO_3$: Electrons per 1 N. |
|---|---|---|
| 1. $HNO_3$,—Nitric Acid (and Nitrates) | $H^+$, $N^{5+}$ $3O^{--}$ | 0 |
| 2. $NO_2$, Nitric Peroxide | $N^{3+}$, $2O^{--}$ | 1 |
| 3. $HNO_2$, Nitrous Acid (and Nitrites) | $H^+$, $N^{3+}$, $2O^{--}$ | |
| 4. NO, Nitric Oxide | $N^{++}$, $O^{--}$ | 2 |
| 5. $N_2O$, Nitrous Oxide | $2N^+$, $O^{--}$ | 4 |
| 6. N, Nitrogen | $N^\circ$ | 5 |
| 7. $NH_3$ (or $NH_4OH$), Ammonia (or its salts) | $N^{---}$, $3H^+$ | 8 |

The student should commit the foregoing table to memory.

### 15. General Facts Concerning the Action of Nitric Acid with Various Reducing Agents.

From the position of nitric acid in the Table of Electromotive Reactions, it is seen that nitric acid reacts with all substances in the left column above line 32, and this is certainly true of all substances beginning with 29 left. Technically, we say:—all these substances in the left column from 29 up are *oxidized* by nitric acid. In all such reactions, the nitric acid is *reduced* to its various products named in the table above. It is seldom that, in any case, only one particular reduction product is formed; however, under particular conditions some particular product is formed *chiefly*. The following general rule connects these conditions with the chief product formed in each case:—the nitric acid is reduced to a greater extent if its solution is more dilute or if stronger reducing agents act upon it. For example—

conc. $HNO_3$+copper gives $NO_2$

dil. $HNO_3$+copper gives NO

dil. $HNO_3$+zinc gives N

very dil. $HNO_3$+zinc gives $NH_3$

The above rule and these examples should be committed to memory and used as a means of predicting the extents of reduction of nitric in other mixtures.

### 16. Nitric Acid Pole Reactions.

The electromotive reactions for the formation of the six different reduction products of nitric acid are expressed by the following equations:

(a) $(H^+, N^{5+}, 3O^{--})+1(-)+1$ extra $H^+=NO_2+H_2O$

(b) $(H^+, N_2^{5+}, 3O^{--})+2(-)+2$ extra $H^+=HNO_2+H_2O$

(c) $(H^+, N^{5+}, 3O^{--})+3(-)+3$ extra $H^+=NO+2H_2O$

(d) $2(H^+, N^{5+}, 3O^{--})+2\times4(-)+2\times4$ extra $H^+=N_2O+5H_2O$

(e) $2(H^+, N^{5+}, 3O^{--}+2\times5(-)+2\times5$ extra $H^+=N^\circ_2+6H_2O$

(f) $(H^+, N^{5+}, 3O^{--})+8(-)+8$ extra $H^+=NH_3+3H_2O$

The equations for the reactions between nitric acid and various reducing agents will now be presented together with experiments in which these reactions take place.

### 17. Demonstration of the Great Oxidizing Tendency of Concentrated Nitric Acid.

**Experiment.**—Secure a porcelain dish, about six or eight inches in diameter, and put into it some tap-water. Secure, in a test-tube, a few c.c. of fuming nitric and a small piece of charcoal. Hold the test-tube with a clamp, warm the nitric acid, and at the same time hold the charcoal, with a pair of tongs, in the flame of a burner until it has ignited. Then, while holding the test-tube over the dish full of water (as a precaution against its breaking!) drop the glowing charcoal into it. The charcoal should burn vigorously in the acid.

This shows that, at high temperatures, nitric acid dissociates so as to form free oxygen. This it can do only by forming N—compounds in which N has a lesser valence than 5, as shown, for instance, by the equation:

$$2HNO_3=H_2O+NO_2+O$$

N—valence $=5$ N—valence $=4$

Since the N in $HNO_3$ actually does this valence changing at high temperatures, it is to be expected that it exerts some of this tendency even at ordinary temperatures.

### 18. The Preparation of Nitric Peroxide.

**Experiment.**—Put a little "scrap" sheet copper into a test-tube and add about 1 c.c. of *concentrated nitric acid to it.* The reddish-brown gas evolved is nitric peroxide—$NO_2$. It is produced by the *least* reduction of nitric acid. Its production under these conditions is all that is to be noted here.

This reaction between copper and concentrated nitric acid is evidently a combination of equation (a), Art. 16.

$$(H^+, N^{5+}, 3O^{--})+1(-)+1 \text{ extra } H^+=NO_2+H_2O.$$

and of the electromotive change of copper,—

$$Cu^\circ = Cu^{++} + 2(-)$$

In order that the electrons formed from $Cu^\circ$ will be taken up wholly by the $HNO_3$, $2HNO_3$ must change while 1 $Cu^\circ$ changes; hence we must multiply the first equation by 2 and obtain,—

$$2HNO_3 + 2(-) + 2H^+ = 2NO_2 + 2H_2O$$

Then, taking the second equation,

$$Cu^\circ = Cu^{++} + 2(-)$$

adding the left sides and the right sides, cancelling the electrons, and adding the extra $NO_3$ ions, we obtain the common form of the equation:

$$2HNO_3 + 1Cu^\circ + 2HNO_3 = 2NO_2 + 2H_2O + 1Cu(NO_3)_2$$

**19. The Preparation and Some of the Properties of Nitric Oxide.**

**Experiment.**—Fit up a flask as for the preparation of hydrogen—with a two-hole rubber stopper, a delivery tube, and a thistle-top funnel, the stem of which extends to the bottom of the flask. Put into the flask about 10 grams of small pieces of sheet copper (scrap!), add about 15 c.c. of water, and then when ready for all that is to follow (see below), add gradually an equal volume of concentrated nitric acid. Collect the gas evolved over water. This colorless gas is nitric oxide, NO:—it is only slightly soluble in water. Fill one wide-mouth bottle (about 500 c.c. capacity) wholly with the gas; but fill a second bottle only one-third full and leave this bottle in the water. Then let the gas bubble through a little of a solution of a ferrous salt (use ferrous-ammonium sulphate). The black compound, of ferrous ion and NO, is used as a means of revealing the presence or absence of nitric acid in mixtures; i. e., in qualitative analysis.

Lower a burning match into the bottle full of nitric oxide,—do this with as little loss of the gas as possible. Then lower into the gas a deflagrating spoon with some well-burning red phosphorus. At low temperatures—such as those produced by the burning match even—the nitric oxide does not dissociate sufficiently to furnish oxygen of such concentration that the match may burn:—but at the higher temperature produced by the burning of the phosphorus, the dissociation of nitric oxide furnishes oxygen of such concentration that the phosphorus may burn.

The other bottle, which is filled only one-third full with nitric oxide, is to be tilted so as to admit some air:—note the formation of nitric peroxide which shows that nitric oxide and oxygen combine to form $NO_2$. Then shake the bottle so as to splash the water up inside of it:—note that the reddish-brown fumes disappear—nitric peroxide dissolves in cold water, forming nitric acid and nitrous acid, according to the equation—

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

Air may be admitted until all the nitric oxide has been used up.

The reaction between dilute nitric acid and copper evidently consists of equation (c), Art. 16, and the equation for the change of copper. Here, $HNO_3$ and Cu must change in the ratio

$$2HNO_3 \quad : \quad 3Cu^\circ$$

in order that the electrons formed from the Cu° may all be used up by the $HNO_3$. Multiplying the corresponding equations by 2 and 3, we obtain—

$$2HNO_3+6(-)+6H^+=2NO+4H_2O$$
$$3Cu^\circ \qquad\qquad =3Cu^{++}+6(-)$$

Adding, cancelling the electrons, and adding the "inactive" $NO_3^-$ ions, we obtain—

$$2HNO_3+3Cu^\circ+6HNO_3=2NO+4H_2O+3Cu(NO_3)_2$$

**20. The Reduction of Nitrates to Ammonia.**

**Experiment.**—Very strong reducing agents (zinc or aluminium) reduce very dilute nitric acid or nitrates to the extreme limit—ammonia. This is most conveniently accomplished as follows:—secure in a test-tube some finely divided aluminium, cover it with a concentrated solution of caustic soda, and add a few drops of dilute nitric acid: it will take a few minutes until a vigorous action has set in, then the presence of ammonia will be noticeable.

The equation for this reaction is the sum of equation (*f*) Art. 16, and of the equation for the electromotive change of aluminium. From the numbers of electrons involved in these changes, it is evident that $3HNO_3$ changes while 8 (Al) change. Hence we multiply the first equation by 3,

$$3HNO_3+3\times 8(-)+3\times 8 \text{ extra } H^+=3NH_3+9H_2O$$

and the second by 8, thus:

$$8Al=8Al^{+++}+24(-)$$

On adding these, we obtain

$$3HNO_3+8Al+24 \text{ extra } H^+=3NH_3+9H_2O+8Al^{+++}$$

To get the final equation, we must add extra ions to change $8Al^{+++}$ to $8NaAlO_2$. This requires $8Na^+$ ions, and 16 $O^{--}$ ions. These and also the 24 extra $H^+$ ions in the equation above, will be supplied if we add 8NaOH and $8H_2O$. Hence adding 8NaOH and $8H_2O$ in place of the 24 extra $H^+$, and putting $8NaAlO_2$ in place of $8Al^{+++}$, we obtain the final form—

$$3HNO_3+8Al+8NaOH+8H_2O=3NH_3+8NaAlO_2+9H_2O$$

In its simplest form, this equation is evidently,—

$$3NaNO_3+8Al+5NaOH+2H_2O=3NH_3+8NaAlO_2$$

**21. Exercise on the Reduction Products of Nitric Acid.**

At the end of Art. 15 definite information was given regarding the reduction products of nitric acid of various concentrations with two representative metals. It is often desired to write the equations for the reaction between a metal and nitric acid of a cer-

tain concentration. A list could be compiled of the reduction products obtained from all the metals—each with nitric acid of various concentrations. But such a list would be quite long and the student would not be able to remember it in its entirety. Hence the student should learn to make an "intelligent guess" as to the probable reduction product of nitric acid of *any* reaction. For this purpose, he should construct a table in the following way:

(1) Divide the metals into three representative groups according to their position in the Electromotive Reaction Table in Art. 5, with zinc, lead, and copper as the representative metals of these groups.

(2) Use three concentrations of nitric acid: concentrated, dilute, and very dilute nitric acid with each group of metals.

(3) Use the data given at the end of Art. 15 to start the table.

(4) Then, carefully fill out the table in the light of what has been learned so far in Arts. 14-20, inclusive.

### 22. The Oxidizing Action of Sulphuric Acid.

Concentrated sulphuric acid is a powerful oxidizing agent. It is used occasionally just like nitric acid to dissolve copper, silver, or mercury,—i. e., metals which do not dissolve in hydrochloric acid or in dilute sulphuric acid by liberating hydrogen gas; and, again like nitric acid, concentrated sulphuric acid does not attack gold or platinum.

Since the main reduction products of sulphuric acid are known to the student, it is advisable to add here the few remarks necessary to inform him concerning the general facts involved in its oxidizing actions.

THE COMPOUNDS OF SULPHUR IN DESCENDING ORDER OF OXIDATION STAGES.

| Order | Common Form of Each Oxidation Stage | Theoretical Elemental Ions | Reduction Electrons per S |
|---|---|---|---|
| 1 | $H_2SO_4$, Concentrated Sulphuric Acid (and Sulphates) | $2H^+$, $S^{6+}$ $4O$ | 0 |
| 2 | $SO_2$, (or $H_2SO_3$), Sulphur dioxide, sulphurous acid, and sulphites | $S^{4+}$, $2O^{--}$ | 2 |
| 3 | S, Sulphur | $S^o$ | 6 |
| 4 | $H_2S$, Hydrogen sulphide, and other sulphides | $2H^+$, $S^{--}$ | 8 |

Weak reducing agents, such as metallic silver, and metallic copper reduce concentrated sulphuric acid the least amount only—i. e., to $SO_2$. Strong reducing agents, such as zinc, reduce it to the greatest extent—i. e., to $H_2S$.

**Experiment.**—Put a little "scrap" sheet copper into a test-tube, cover it with concentrated sulphuric acid, warm the mixture until reaction ensues:—note the odor of the escaping gas. Repeat this trial with granulated zinc in place of copper.

### 23. The Pole Reactions for Sulphuric Acid.

The following equations express the reduction of $H_2SO_4$ to its reduction products:—

(a) $H_2SO_4+2(-)+2H^+=SO_2+2H_2O$
(b) $H_2SO_4+6(-)+6H^+=S+4H_2O$
(c) $H_2SO_4+8(-)+8H^+=H_2S+4H_2O$

The equation for the reaction between copper and sulphuric acid is obtained by adding equation (a) above to the equation for the change of copper because 1Cu produces as many electrons—i. e., 2—as $1H_2SO_4$ uses up to form $SO_2$. The addition of these equations gives—

$$Cu+H_2SO_4+2H^+=Cu^{++}+SO_2+2H_2O$$

Adding the inactive $SO_4^{--}$ ions, we obtain—

$$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$$

To obtain the equation for the reaction between Zn and $H_2SO_4$, add together equation (c) above and —

$$4Zn=4Zn^{++}+8(-)$$

### 24. The Reaction Between Concentrated Sulphuric Acid and the Three Halides.

The fact that stronger reducing agents reduce such oxidizing agents as concentrated sulphuric acid to a greater extent than weaker reducing agents is shown well by the action between concentrated sulphuric acid and chlorides, bromides, and iodides, respectively. It is evident from the position of the latter in the table of battery poles that their tendency to form the free halogens *increases* in the order in which they are here named—chlorides, bromides, iodides—and in accordance with this we find that in the action of concentrated sulphuric acid with chlorides there is no oxidation or reduction, with bromides there is formation of bromine and slight reduction of the sulphuric acid (to $SO_2$), while with iodides there is formation of iodine and very extensive reduction of the sulphuric acid (to sulphur, or to hydrogen sulphide even). For a demonstration, try, in test-tubes, small amounts of potassium iodide and of potassium bromide, respectively, with a little concentrated sulphuric acid. The action between concentrated sulphuric acid and chlorides may be remembered from earlier experiments.

With the data indicated in the foregoing, balance the equations which take place in these two test-tube trials.

### 25. The Oxy-Halogen Compounds.

The only compounds of the halogens dealt with so far in these oxidation-reduction reactions are the halides—which represent a lower oxidation stage than the free halogens. Besides these, there are other compounds of the halogens, such as chlorates and hypochlorites (bleaching powder!), in which the halogens exist in *higher oxidation stages* than that corresponding to the free halogen, and these are to be considered here.

THE COMMON HALOGEN COMPOUNDS IN DESCENDING ORDER OF OXIDATION STAGES.

(X stands for Cl, Br, or I.)

| Order | Common Form of Each Oxidation Stage | Theoretical Elemental Ion | Reduction Electrons per X |
|---|---|---|---|
| 1 | $HXO_4$ Perhalate (e. g. perchlorate, $KCl\ O_4$) | $H^+, X^{7+}, 4O^{--}$ | 0 |
| 2 | $HXO_3$ Halate (e. g. chlorate, $KCl\ O_3$) | $H^+, X^{5+}, 3O^{--}$ | 2 |
| 3 | $HXO_2$ Halite (e. g. chlorite, $KCl\ O_2$) | $H^+, X^{3+}, 2O^{--}$ | 4 |
| 4 | HXO, Hypo-halite (e. g. hypo-chlorite $KCl\ O$) | $H^+, X^+, O$ | 6 |
| 5 | Free halogen (e. g. Cl) | $X^o$ | 7 |
| 6 | HX, Halide (e. g. chloride, KCl) | $H^+, X^-$ | 8 |

The only oxy-halogen compounds which are of common occurrence are the halates and the hypo-halites—more particularly the chlorates, and the hypo-chlorites. In the formation of these compounds, chlorine, bromine, and iodine are so nearly alike that it is necessary to illustrate with only one of these elements.

The halates (e. g., $KClO_3$) are very stable salts, and strong oxidizing agents. Potassium chlorate is used in many cases where oxidizing agents are needed. In most of these reactions it is reduced to the chloride stage (6 electrons required per $KClO_3$!). The hypo-halites (e. g., bleaching powder), are also strong oxidizing agents, and on this account bleaching powder is one of the most valuable and widely used disinfectants for the purification of potable water, sterilization of sewage, etc. In such reactions, it is mostly reduced to the chloride stage (2 electrons necessary per NaClO).

### 26. Fundamental Facts in the Behavior of Free Halogens and Hypohalites.

(a) When a halogen is placed into pure water, a slight reaction takes place, yielding small quantities of hydrogen halide and

the hypohalite acid, the principal part of the dissolved free halogen remaining in the solution *as such*. Illustrating with chlorine, the reaction is

$$Cl_2^\circ + H_2O \rightleftarrows HCl + HClO$$

This reaction is a reversible reaction, which reaches equilibrium when most of the chlorine is in the form of $Cl_2^\circ$. If the solution is acidified, the equilibrium is shifted farther to the "left"; i. e., with the formation of more of the substances on the left-hand side of the equation above. These are *observed* facts.

(b) When a halogen is placed into a solution of a strong base, the free halogen reacts almost completely to form the halide and the hypohalite, very little free halogen remaining in solution *as such*. Illustrating again with chlorine, the reaction can be written

$$Cl_2^\circ + 2NaOH \rightleftarrows NaCl + NaClO + H_2O.$$

This, again, is a reversible reaction with the equilibrium placed far to the "right"; i. e., most of the chlorine is present in the form of compounds—the substances on the right of the equation above. This, again, is an *observed* fact.

What, then, is the fundamental difference in the nature of the two solutions (*a* and *b*) that causes this marked change in the point of equilibrium and in the quantities of halide and hypohalite formed in the two cases? Consider the reaction (X representing a halogen):

$$X^\circ_2 + H_2O \rightleftarrows H^+ + X^- + HXO$$

The products of the equilibrium *on the right* are the $H^+$, the halide ion—$X^-$, and the hypohalous acid—HXO. In solution (a), there are a large number of $H^+$ ions present; in solution (b), there are extremely few $H^+$ ions present. The difference in behavior of the two solutions, then, lies in the difference of the $H^+$ ion concentrations, the equilibrium being "held" on the right by the $X^-$, the HXO, and *by the hydrogen ions*. If these $H^+$ ions are neutralized by the addition of $OH^-$ from a base, the equilibrium will shift toward the "right," causing the free halogen to disappear (as in *b*); if the $H^+$ ions are increased or not destroyed (as in *a*), the equilibrium will shift toward the "left." Schematically, this can be represented by the following tabular views:

$$X_2^\circ + H_2O \rightleftarrows H^+ + X^- + HXO$$

| | |
|---|---|
| *Fact:* When the $(H^+)$ is large, then the $(OH^-)$ is small, and most of the halogen is in the free form—$X_2^\circ$. | *Fact:* When the $(H^+)$ is small, then the $(OH^-)$ is large, and most of the halogen is present as $X^-$ and HXO. |

*Conclusion:* If free halogen is to be changed to halide and hypohalite, put the halogen into a basic solution (free $OH^-$ present); and if hypohalite is to be changed to free halogen, make the hypohalite solution acidic (free $H^+$ ions present).

*Note:* The hypohalous acids (hypochlorous, hypobromous, and hypoiodous acids) are weak acids; i. e., they are only slightly ionized in solution.

**Experiment.**—To one c.c. of sodium hydroxide solution add a few drops of bromine water and note how its color disappears (through the formation of NaBr+NaBrO, which are colorless!).

The equation for the above reaction is

$$Br_2° + 2NaOH = NaBr + NaBrO + H_2O.$$

This reaction presents the novel feature of the same substance acting as the oxidizing and also as the reducing agent: 1 *Br* is oxidized to the $Br^+$ stage, and the other one is reduced to the $Br^-$ stage (ratio 1:1). In other words, the equation above is the sum of the following electromotive changes:

$$Br_2° = 2Br^+ + 2(—)$$
$$Br_2° + 2(—) = 2Br^-$$

On addition: $2Br_2° = 2Br^+ + 2Br^-$

or $Br_2° = Br^+ + Br^-$

Addition of one molecule of water gives the final form:

$$Br_2° + H_2O = (H^+, Br^-) + HBrO.$$

**27. The Fundamental Facts Involved in the Formation of Halates.**

The formation of halates (of the general formula $HXO_3$ or $MXO_3$) from hypohalites depends upon the reaction of free hypohalous acid with the hypohalite ion, $(XO)^-$, from a salt of hypohalous acid. This condition can exist only in a practically neutral or faintly acidic solution (or in the contact layer between acid and basic solutions!). The equation representing this change is

$$2HXO + (XO)^- = (XO_3)^- + 2H^+ + 2X^-$$

The condition imposed upon this reaction (i. e., almost neutral or faintly acidic solutions) can best be obtained:

(a) by a solution of sodium bicarbonate acidified with carbonic acid (a weak acid!), or

(b) by a solution or suspension of $Mg(OH)_2$ or $Ca(OH)_2$—very slightly soluble bases.

The addition of a hypohalite to such a solution will produce a halate and a halide. A rise of temperature produces an increase in the velocity of reaction; hence such solutions are heated.

In actual practice, the free halogen is placed in a solution hav-

ing the composition of either (a) or (b). The formation of the halide and hypohalite (HXO and NaXO) takes place first according to the reactions described in Art. 26; while the additional step, leading to the formation of the halate, is

$$2HXO + (XO)^- = (XO_3)^- + 2H^- + 2X^-$$

$$\text{or} \quad 2HXO + NaXO = NaXO_3 + 2HX.$$

The halogen acid produced by this reaction is naturally neutralized as soon as produced by more of the free base in solution.

This reaction, again, presents the feature of the same element acting in both capacities: as a reducing agent and as an oxidizing agent. Illustrating with the hypochlorite, the following electromotive changes are encountered:

$$Cl^- = Cl^{5+} + 4(-)$$

$$2Cl^- + 4(-) = 2Cl^-$$

On addition: $Cl^- + 2Cl^- = Cl^{5+} + 2Cl^-$

The complete equation for the change that would take place in solution (a) would be

$$2HClO + NaClO = NaClO_3 + 2HCl$$

while the one for solution (b) would be

$$4HClO + Mg(ClO)_2 = Mg(ClO_3)_2 + 4HCl.$$

Naturally, the HCl produced as per above equations reacts immediately as follows:

$$\text{in (a)} \quad 2HCl + Na_2CO_3 = 2NaCl + H_2O + CO_2$$

$$\text{in (b)} \quad 2HCl + Mg(OH)_2 = MgCl_2 + 2H_2O$$

**Experiment.**—Make a mixture 35 grams of CaO and 125 c.c. of water, put it into a flask, heat it to the boiling point, and keep it hot while passing 35 grams of chlorine into it gradually. To produce this chlorine, put 125 grams of good bleaching powder and 50 c.c. of water into a flask fitted as for the preparation of carbon dioxide and add to it, gradually, about 150 c.c. of concentrated hydrochloric acid.

After having passed all the available chlorine into the lime mixture, filter it while it is hot, then add 15-20 grams of crystals of potassium chloride, and stir the mixture until they are dissolved. Then cool it: crystals of potassium chlorate will separate from the cooled solution because this is the least soluble combination of ions in the mixture.

The reaction between the chlorine and the hot lime water takes place according to the following equation which is the sum of the several independent equations mentioned above:—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

**28. The Oxidizing Action of an Acidified Permanganate Solution.**

A solution which contains a permanganate and some free acid ($H_2SO_4$) reacts with the same substances with which nitric acid

reacts—i. e., with all the substances above 30 left in the column of the Table of Electromotive Reactions. The equation for the electromotive reaction of the acidified permanganate solution is given in Note 6, appended to the *Table*.

The "key" to this electromotive change or "oxidizing action" of the permanganic acid is the fact that $Mn^{7+}$ (in $HMnO_4$) changes to $Mn^{2+}$ (in $MnSO_4$, $MnCl_2$, etc.), or in symbols—

$$Mn^{7+}+5(-)=Mn^{2+}$$

Since $Mn^{7+}$ is accompanied by $1H^+$ and $4O^{--}$ ions, we have—

$$(H^+,\ Mn^{7+},\ 4O^{--})+5(-)+7 \text{ extra } H^+=Mn^{2+}+4H_2O$$

By combining this equation with the equations of the electromotive changes of various "reducing agents" (e. g., $FeSO_4$, or Zn°, or $H_2S$, or HCl, etc.), the ordinary equations for the oxidation-reduction reactions of such mixtures are readily derived.

**Experiment.**—Put a few c.c. of a solution of a permanganate into a test-tube, add 5 to 10 drops of dilute sulphuric acid, and add, drop by drop, a solution of a ferrous salt (e. g., $FeSO_4$) until the pink color of the permanganate has disappeared. The change of the color is due to the fact that the substances *produced* are relatively colorless.

Repeat by adding $SnCl_2$ solution in place of ferrous sulphate solution.

Repeat, passing hydrogen sulphide through the acidified permanganate solution instead of adding ferrous sulphate solution.

Derive the equation for the changes in these mixtures.

**29. The Oxidizing Action of an Acidified Chromate Solution.**

A solution which contains a chromate and some free acid ($H_2SO_4$) reacts with the same substances with which acidified permanganate solution reacts. The equation for the electromotive reaction is given in Note 5 to the Table of Electromotive Reactions. The "key" to this reaction is the fact that $Cr^{6+}$ (in $H_2Cr_2O_7$) changes to $Cr^{3+}$, or in symbols—

$$Cr^{6+}+3(-)=Cr^{3+}$$

Note 5 (appended to the Table) gives the complete equation for this electromotive change. Derive the *ordinary* equation for the oxidation-reduction reaction between this acidified bichromate and $H_2S$. Also, pass $H_2S$ into hot solution containing $H_2SO_4$ and a bichromate, and note the formation of free sulphur, and the change of color from reddish-yellow to green: the latter is due to the change of chromium in chromates ($Cr^{6+}$) to chromium in chromic *salts* ($Cr^{3+}$). The latter are similar to aluminium salts and ferric salts.

**30. Review Questions on Chapter XII.**

1. The test for the nitrate ion is the reaction between $FeSO_4$ and dilute $HNO_3$. Figure out the complete equation for this reaction.

2. When hydrogen sulphide is passed into an acidified solution of potassium permanganate, the violet color of the permanganate disappears and the solution becomes milky. Write the equation for this reaction.

3. A little sulphur dioxide is passed into clear hydrogen sulphide water. The solution becomes milky. Write the complete equation.

4. A solution of sodium iodide and sodium bromide is electrolyzed. What are the products of electrolysis at each pole? Why?

5. A solution of cadmium and nickel nitrates is subjected to electrolysis, the applied voltage beginning with zero value and is gradually increased to such a value that a metal begins to be deposited. What metal will be deposited? Why?

6. Concentrated sulphuric acid is poured on potassium iodide crystals: the solution is turned reddish-violet. Write the equation for the change that has taken place.

7. Iron is added to a solution of silver nitrate. Describe what would happen and write the equation for the change.

8. To an acidified solution of hydrogen sulphide some orange-colored potassium dichromate is added. The solution turns green. Write the equation for the reaction.

## CHAPTER XIII.

## THE FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY AND THE CHIEF TYPES OF ORGANIC COMPOUNDS.

### 1. The Two Great Classes of Organic Compounds.

Organic chemistry is the chemistry of the carbon compounds and is concerned with combinations of carbon with hydrogen, oxygen, nitrogen, sulphur, phosphorus, and the halogens.

On account of important differences in properties, all organic compounds are divided into two great classes: the "straight-chain" or *fatty* compounds, and the "cyclic" or *aromatic* compounds. The former class includes among other substances the hydrocarbons found in petroleum, the sugars, oils and fats of animal and vegetable origin, etc., and the latter includes the "coal tar" dyes, carbolic acid, naphthalene, i. e., compounds obtained from coal tar or from coal tar distillates. The straight-chain compounds will be presented first, and we will begin with the simplest straight-chain compounds, the saturated hydrocarbons, or the paraffin series of hydrocarbons. They are also called the Methane or Marsh Gas series from the lowest member of the series, which is $CH_4$, Methane or Marsh Gas.

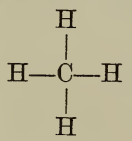
### 2. The Fundamental Ideas Underlying the Structure Theory of Compounds.

Organic chemistry owes its wonderful development to the *structure theory,* according to which the atoms in organic compounds are tied together by *bonds,* which in number are equal to the valences of the elements. The special fundamental ideas employed in the structure of carbon compounds are these:

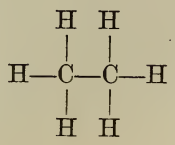
1. The carbon atom always has a valence of 4.
2. A carbon atom may be united to another carbon atom, and this in turn to another and so on without limit.
3. Two carbon atoms may be directly connected by one, two or even three bonds.

In accordance with these fundamental ideas, the structure of the hydrocarbons of the marsh gas series is represented as follows:

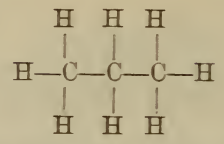
Methane, $CH_4$



Ethane, $C_2H_6$



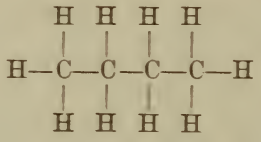
Propane, $C_3H_8$



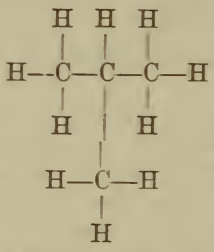
Note (1) that in every instance there are four lines, which represent bonds, or valences, extending out from each C; (2) that in molecules having more than one C, the C's are directly united by bonds.

Since H has one bond only, it is impossible to connect the atoms in the above molecules in any other manner than that shown and still give each carbon four valences.

However, in the following compounds there are several different structural representations possible. Thus with $C_4H_{10}$, we have either



or



This theoretical prediction of the existence of two different compounds, both of which have the composition $C_4H_{10}$ agrees with the fact that two such compounds are actually known, and only two are known. They have the same composition but different properties.

An inspection of the above formulae reveals that the Marsh gas or open-chain compounds obey the general series formula $C_nH_{2n+2}$. The table below lists the boiling points of a few of this series, in all of which the C's are all in a *straight* chain:

| | | |
|---|---|---|
| Methane | $CH_4$ | —164°C |
| Ethane | $C_2H_6$ | —89.5 |
| Propane | $C_3H_8$ | —37.0 |
| Butane | $C_4H_{10}$ | +1.0 |
| Pentane | $C_5H_{12}$ | +35.0 |
| Hexane | $C_6H_{14}$ | +71.0 |
| Heptane | $C_7H_{16}$ | +99.0 |
| Hexadecane | $C_{16}H_{34}$ | +287.5 |

It becomes evident from the above table that as the number of carbons in the molecule increases, the boiling point rises. The first four are gases at room temperature; the members from pentane to hexadecane are liquids; while the members starting with hexadecane are solids.

**3. Exercise.**

Figure out in the manner outlined in the preceding article all possible compounds of the formula $C_5H_{12}$ differing in structure. *Ditto* for $C_6H_{14}$.

**4. Chief Property of the Paraffins: Inactivity.**

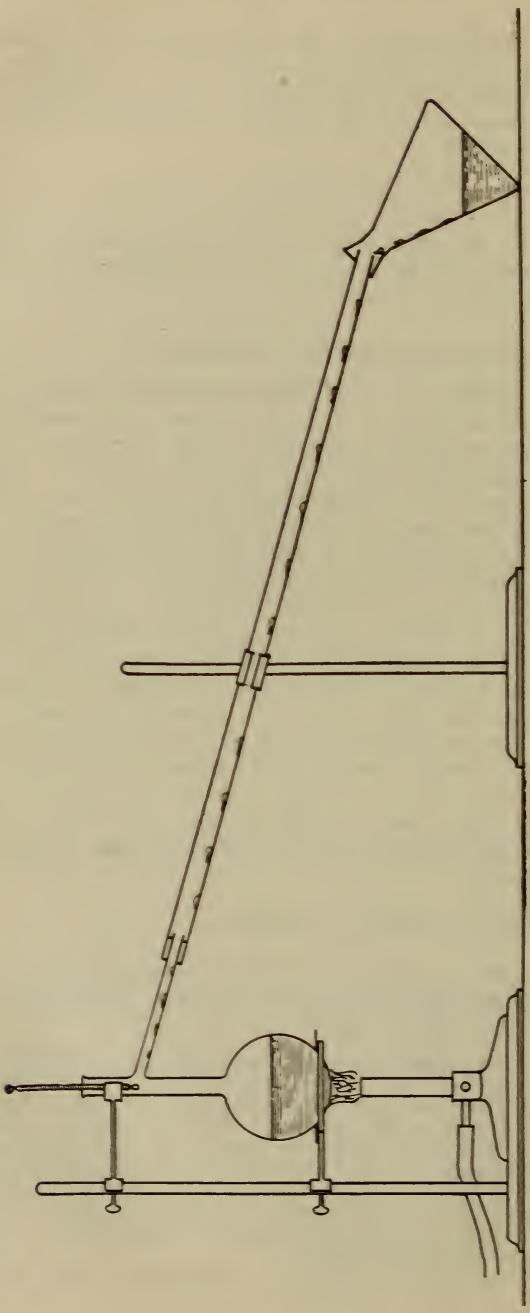
The name *paraffin* is derived from the French and means "no affinity," and it was given to the hydrocarbons of the paraffin series to indicate their chief characteristics. They react with very few reagents, and generally only slowly with any reagents. They are also called *saturated* hydrocarbons, because they do not *unite directly with any substance* (see unsaturated hydrocarbons). Their marked chemical indifference, or stability, or non-reactivity, makes them specially useful wherever such a property is desired, as in the lubrication of bearings and in the oil wiping of machinery, for either of which purposes vegetable oils are utterly unsuitable. Paraffin is frequently melted into wood and into stone and cement to protect them against moisture (water proofing) and chemical agencies. Thus limestone has been protected in smoky cities (Pittsburgh) against the sulphuric acid formed from the sulphur in the coal. The obelisk known as Cleopatra's Needle, in Central Park, New York, has been protected by impregnation with paraffin, and plaster of Paris casts are thus made water proof. In the latter case the objects are painted with a solution of paraffin in benzine or gasoline.

**5. The Distillation of Crude Petroleum.**

In order to become acquainted with the commercial preparation and the common properties of some of these compounds, distill some crude petroleum as follows:

Secure a distilling flask of about 250 c.c. capacity. Fit it with a 360-degree thermometer, and with a wide piece of glass tubing for an "air" cooled condenser (see figure). Secure a piece of asbestos board 6x6 inches and cut a hole in the center 2 inches in diameter. Place this on the ring of a ring stand, clamp the flask to the ring stand, grasping the flask at the uppermost part of the neck, put any suitable object under the condenser tube for its support, and allow its delivery end to extend into a small flask. If a clamp is used to hold the condenser tube, as in the figure, then wads of folded paper should be placed between the jaws of the clamp and the glass tube.

Begin by heating the oil cautiously. If water is present, the upper



Distillation with an Air Condenser

part of the flask may have to be heated at the same time by a separate flame in order that the water will not condense there. The condenser tube should be placed at such an angle that the condensed liquids will run out quickly. When the temperature has reached 200 degrees, change the receiver and collect the portion coming over between 200 and 300 degrees in a clean, dry flask. Note the color of the distillates; note the color and contrast it with that of the crude oil. The distillates obtained by two or three students should be poured together to get enough to make a specific gravity determination. If the amount of distillate is too small to use a "hydrometer," then a specific gravity balance should be employed. What is the specific gravity of this distillate? How does it compare with that of the original oil?

**6. Experiment on the Refining of Kerosene.**

Each student should then take his portion of the distillate and proceed with it as follows:

(a) *Removal of Sulphur:* Put a few c.c. of the distillate into a dry test-tube, add a little yellow lead oxide, and heat the mixture. A blackening of the solid powder shows the formation of lead sulphide. Sulphur in kerosene, etc., is objectionable because it burns to sulphur dioxide, and is eventually oxidized to sulphuric acid in the air. Commercially, the sulphur is removed by treating the distillate with copper oxide or lead oxide, and then redistilling it.

(b) *Removal of Unsaturated Hydrocarbons:* Put the remainder of the distillate into a dry flask, add one-fifth of its volume of concentrated sulphuric acid, and shake the mixture vigorously. Set it aside until the two portions have separated thoroughly, decant the supernatant liquid into another flask, add distilled water, shake and then decant the oil as completely as possible from the water. Add next some concentrated sodium hydroxide solution, using of it about 5 to 10 per cent of the volume of the oil. Shake as with the sulphuric acid, decant and wash with water as before. The resulting oil should be clear, colorless and of a sweet odor. This treatment removes the tarry matter which colors the oil, and also the small amount of ill-smelling compounds present. Clean all vessels by rinsing them out repeatedly with small quantities of gasoline, and either wiping them dry finally or allowing them to drain until perfectly dry. Reserve a small quantity of the refined oil for use in the experiment below.

The distillates obtained below 300° C. can be separated into several quite distinct portions by a more careful fractional distillation. The products obtained are given below, together with their most probable composition.

| Name. | Constituents. | B. P. (760mm.) | Use. |
|---|---|---|---|
| Petrolic Ether | petane and hexane | 30°– 70°C. | solvent |
| Gasoline | hexane and heptane | 70°– 90° | fuel |
| Naphtha | heptane and octane | 90°–120° | solvent and fuel |
| Benzine | octane and nonane | 120°–150° | solvent |
| Kerosene | decane—pentadecane | 150°–300° | illuminating oil |

The distillates obtained from crude petroleum above 300 degrees are heavier and thicker than kerosene, and are called lubricating oils. The lightest of these are called "spindle oils," the middle grades "machinery oils," and the heaviest "cylinder oils."

At still higher temperatures, vaseline ($C_{19}$ $H_{40}$ to $C_{21}$ $H_{44}$) is obtained. When paraffin is present in the crude oil, it is extracted from the lubricating oil and vaseline oil distillates by *chilling* these: the solid paraffin separates (crystallizes out) and is filtered off. Crude oils which furnish paraffin are said to have a "paraffin base." In Texas, the Corsicana oils, the Thrall oils, and the Electra Field oils have a paraffin base, but the Beaumont oils have an "asphalt" base, and they yield no paraffin. The Ranger and Burkburnett oils have a mixed base, yielding both paraffin and asphalt, the ratio of paraffin to asphalt being about 60 to 40. *Asphalt* is a non-crystallizing, pitchy, or gum-like substance in the oil, which remains in the still until it is completely destroyed, leaving a solid carbon residue. If the distillation is discontinued at 300 degrees C. or slightly above, the residue from *asphaltic* oils forms an excellent *binding* material for road-building. Its value as a road-building material depends upon the per cent of *binder* or asphalt in it, and this is "measured" in a sense by a "pulling" test. In Texas, many refineries do not distill beyond 300 degrees C., and sell the residue for fuel oil.

### 7. A Test for Lubricating Oils: Viscosity.

A lubricating oil is valuable on account of its property to form and maintain a film of oil between the two surfaces in contact. A light oil, with little "body," is rapidly squeezed out by heavy bearings, and hence does not prevent friction. The less easily an oil *flows,* the less easily will it be squeezed out; hence, a measure of the usefulness of a lubricating oil for any definite purpose is the determination of its viscosity at the temperature at which it is to be used. The method is outlined below:

Take a 25 c.c. or 50 c.c. pipette, and by means of a gummed label mark a point on the stem just below the bulb. Then fill the pipette with water, and note the time required for the pipette to empty from the mark above the bulb to the mark below the bulb. Dry the pipette by warming it above a flame and sucking air through it. Then determine the time required for an oil sample to flow out of this pipette. This period of time, divided by the time required for water to flow out, gives the viscosity. Secure a sample of lubricating oil and measure the viscosity. Then clean the pipette.

### 8. Flash Point.

In former years kerosene had to be examined for its flash point, because there was very little sale for gasoline, and hence as much of this as possible was left in the kerosene. At present there is practically no danger from this source, because gasoline is more valuable than kerosene. The flash points of kerosene found in the Texas markets at present vary from 84 degrees F. to 102 degrees F. In Texas a "minimum" flash point of kerosene is not fixed by law.

Secure a small evaporating dish about 3½ inches in diameter, and a second one a little larger. Put some sand into the larger one, and fit the smaller one within it, so that the two are separated everywhere by a layer of sand. Place these two dishes on the asbestos board with a 1½-inch hole in it, fill the inner dish with a thin lubricating oil, and suspend a thermometer so that the bulb of the thermometer is immersed in the oil. Heat the oil with an adjustable flame so that the temperature rises uniformly a few degrees (2-4) per minute. By means of another burner apply a very small flame to the surface of the oil once every minute. The temperature with which a flame first flashes across the surface of the oil without continuing to burn is the flash point. At a slightly higher temperature the flame will continue to burn; this is the burning point.

The term *gasoline* is somewhat indefinite as to its composition. The ever increasing demand for gasoline for motor purposes naturally leads producers to include as much of the kerosene fraction with the gasoline as possible, and the gasoline has consequently become of poorer quality for a number of years. In order to check the indiscriminate addition of higher boiling fractions, the Thirty-sixth Legislature of Texas passed the following law (Senate Bill 212), of which the two sections dealing with specifications are included:

"Section 6. For the purpose of this act the word *gasoline* whether used alone or in connection with other words shall apply only to the petroleum products complying with the following minimum requirements:

(a) Boiling point must not be higher than 60° C. (140° F.).

(b) Twenty per cent of the sample must distill below 105° C. (221° F.).

(c) Forty-five per cent must distill below 135° C. (275° F.).

(d) Ninety per cent must distill below 180° C. (336° F.).

(e) The end or dry point of distillation must not be higher than 220° C. (428° F.).

(f) Not less than ninety-five per cent of the liquid will be recovered from the distillation.

(g) Gasoline is to be of high grade, refined and free from water and all impurities, and it shall have a vapor tension not greater than 10 pounds per square inch at 100 degrees Fahrenheit temperature.

"Section 7. The apparatus and methods of conducting all tests and arriving at proper standards of gasoline and other products under this act shall be those now or herafter authorized and used by the U. S. Bureau of Mines."

Ordinary gasoline on the market has a specific gravity of 64 to 68 degrees Beaumé (which corresponds to specific gravity of 0.721 to 0.707). If the official tests for gasoline cannot be conveniently made, it is well to test the specific gravity, for the heavier gasolines are, in general, less valuable.

NOTE.—The Beaumé specific gravity scale, although very unscientific, is used so much in commerce that a word of explanation

will not be out of place here. There are two distinct scales: one for liquids heavier than water and another for liquids lighter than water. The first was designed by dissolving 15 parts of salt in 85 parts of water at 12.5 degrees C. The point to which the spindle sinks in this solution is marked 15 degrees Bé., and the point to which it sinks in water is marked 0 degrees Bé. The scale for liquids lighter than water is designed thus: Ten parts of salt are dissolved in 90 parts of water, and the point to which the spindle sinks in this is marked 0 degrees Bé., while the point to which it sinks in pure water is marked 10 degrees Bé. Hence on this latter scale the number of degrees increases as the specific gravity decreases, while on the scale for liquids heavier than water the number of degrees increases as the specific gravity increases.

In order to facilitate the conversion of Beaumé readings into specific gravity readings, the following formulæ are used:

(a) For *heavy liquids:* Sp. Gr. $=145\div(145-\text{deg., Bé.})$.

(b) For *light liquids:* Sp. Gr. $=140\div(130-\text{deg., Bé.})$.

**9. Unsaturated Hydrocarbons.**

The two-C member of the paraffin series has the composition $C_2H_6$, and it has the characteristic property of the paraffins,—namely, of being comparatively non-reactive. There is another two-C compound which occurs in illuminating gas, but which has the composition of $C_2H_4$ and is called ethylene. In order to represent its structure in accordance with the idea that carbon is always tetravalent, we write—

$$\begin{array}{ccccc} H & - & C & = & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

It is very reactive. Thus it combines very quickly with bromine to form a compound of the composition $C_2H_4Br_2$. More bromine than corresponds to this formula is not taken up readily. In order to express the structure of this compound, we write—

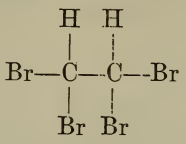
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Br & & Br & & \end{array}$$

On comparing this with the structural formula of $C_2H_4$ we note that the second bond between the C's has been broken and the two Br's have been attached by means of the bonds thus made available.

Another two-C compound, which is well known in daily life, has the formula $C_2H_2$—acetylene. Its structures must be written thus—

$$H-C\equiv C-H$$

in order to represent carbon as tetravalent. This substance takes up bromine or chlorine and many other reagents very readily. With bromine it forms a compound of the formula $C_2H_2Br_4$, but more bromine than corresponds to this formula is not taken up. That 4Br is the maximum amount that can be taken up is rendered plausible by writing the structure of this compound thus—



which shows that it has a structure similar to the inactive compounds of the paraffin series.

Compounds which like the $C_2H_4$ and the $C_2H_2$ above combine readily and direct with other substances are called *unsaturated* compounds: they always have either a double or triple bond in their structural formula. But substances similar to the paraffins in structure do not combine with other substances, and they are hence called saturated compounds. The C's in saturated compounds are connected by single bonds only, in their structural formulae.

**10. An Illustration of the Reactivity of Unsaturated Compounds.**

The marked tendency of unsaturated compounds to form "addition compounds" can be readily demonstrated as follows:

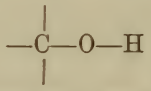
Secure some bromine water; then drop a fragment of calcium carbide into a little distilled water, and pour some of the water, thus saturated with acetylene, into the bromine water, until the color of the bromine has disappeared. Acetylene combines with bromine to form $C_2H_2Br_4$. Note how rapidly the reaction takes place. Write the structural formula of this resulting compound.

Acetylene can be burned without the formation of soot if it issues from a very fine opening. Great care must be exercised in handling the gas, because with copper compounds such as may be formed on brass fittings it forms a very explosive carbide, and mixed with air in *any* proportion it forms a very violently exploding mixture. (The latter is not true of the other common combustible gases: their mixture with air are not explosive if either ingredient is present in small amounts.) For the above reason, the use of tanks full of compressed acetylene gas cannot be safely used for lighting purposes. But the gas may be compressed into *acetone,* in which liquid it is very soluble. This liquid does not dissolve air or oxygen appreciably and hence contains no explosive mixture. Tanks full of this solution, called "Prestolite," were formerly used extensively for lighting purposes on automobiles, and are still used in the lighting of country homes. The prin-

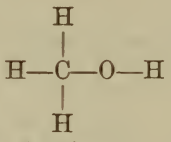
cipal use today, however, lies in its application in the welding and cutting of iron and steel. When acetylene is burned with oxygen in an oxy-acetylene torch, the temperature of the flame is extremely high and will melt its way through a steel plate several feet wide or through a six-inch steel shaft in a very short while. A great deal of the repairing of broken steel castings is done today by means of the oxy-acetylene torch.

**11. Alcohols.**

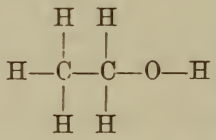
The term *alcohol* is a general one which denotes compounds in which an OH group is attached to a carbon atom with one bond while the other three bonds of this carbon atom are connected to other carbon atoms or to hydrogen atoms. Whenever a compound has this grouping—



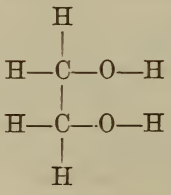
with the three bonds "which are here left open" connected to H or to C atoms, then it is an *alcohol.* Thus the structure of the simplest alcohol in existence, wood alcohol, or methyl alcohol, is written as follows:



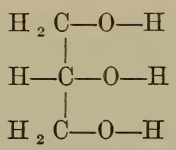
and the compound of the structure—



is also an alcohol (vinous alcohol or ethyl alcohol) because the carbon on the right in the figure shows the characteristic alcohol group. This group can occur on more than one carbon in the compound. Thus glycol $(CH_2OH)_2$ has the structure—



and it is chemically just as much an alcohol as the substances just mentioned above. The same is true of glycerine,



Note the condensed form of the structural formula here given: from now on structural formulae will be written in as condensed a form as is compatible with clearness.

The monovalent radicals ($CH_3$, $C_2H_5$, $C_3H_7$) obtained by taking away *one* H from the paraffin hydrocarbons ($CH_4$, $C_2H_6$, $C_3H_8$) are named by putting "yl" in place of "ane" in the name of the original hydrocarbon—e. g.:

Methyl, $CH_3$, is named from methane, $CH_4$;

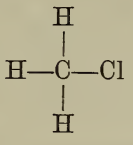
Ethyl, $C_2H_5$, is named from ethane, $C_2H_6$.

The general term for such a radical is *alkyl*.

**12. The Connection Between Hydrocarbons and Alcohols.**

Theoretically the alcohols are the first derivatives obtainable by oxidizing hydrocarbons, but it is practically impossible to make alcohols this way.

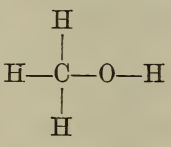
For scientific purposes, alcohols have been made direct from hydrocarbons, but the process is too expensive to be used commercially. However, this manner of formation of alcohols—direct from their hydrocarbon—is the means by which the structure of the alcohols was recognized—in a manner shown in the following example: by treating methane, $CH_4$, with chlorine under suitable conditions, a compound of the formula—



is obtained according to the equation:—

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

and if this is treated with moist silver oxide (which may be considered to be AgOH), then by metathetical reaction OH is put in place of Cl, and hence the resulting compound should have the structure—



The compound thus obtained is identical with the compound ob-

tained from the dry distillation of wood, and which is known as wood alcohol, or methyl alcohol. By means of the above scientific preparation of the various alcohols from hydrocarbons, the formulae and structures of the alcohols have been thoroughly proven, and on account of this theoretical relation to the hydrocarbons the alcohols are here considered next in order; however, it should be noted that in their commercial preparation there is no direct connection between the hydrocarbons and the alcohols.

### 13. Properties of Wood Alcohol (or Methyl Alcohol).

Commercial methyl alcohol is often slightly yellowish in color, and has generally a disagreeable odor. Taken internally, it acts as a poison, which, according to its concentration or the quantity taken, will produce severe headaches and nausea, or death. Four ounces taken internally in any form are said to produce either death or permanent blindness in most instances. Even its vapor produces these baneful results, particularly blindness, and hence its use in industry, as a solvent for lacquers or varnishes, and for other uses, is to be deprecated, and the use of vinous alcohol to be advanced. When pure it boils at 66.7 degrees C. and has a specific gravity of .7995 at 15 degrees C. It is perfectly miscible with water, vinous alcohol, and ether; and it is an excellent solvent for fats, oils, resins, and is hence used in varnish making. It is also used as a fuel, and in some cases it is used as a denaturant of vinous alcohol, and it is used to make formalin.

### 14. The Preparation of Ethyl Alcohol by Fermentation.

Secure about 30 grams of glucose or of some cheap molasses, dissolve it in about 150 c.c. of water, add some yeast, shake the mixture thoroughly and warm it slightly (not above 40° C.). Put the mixture into a flask, leave this uncorked, and set it aside in your desk for two or three days, or until the slow evolution of a gas which takes place at first has practically ceased. Test for the presence of ethyl alcohol by means of the following test.

### 15. The Iodoform Test for Ethyl Alcohol.

A qualitative test for ethyl alcohol is made as follows: Warm a little of the solution to be examined, add a few iodine crystals and then add enough sodium hydroxide solution to decolorize the mixture. After the lapse of a short while, a yellow precipitate of iodoform ($CHI_3$) will appear if alcohol is present in the sample.

The reaction may be considered to take place as follows:

$$\begin{array}{lcl} CH_2OH + & 2I + OH & \\ | & | & = \\ CH_3 & + \; 6I + H & \end{array} \quad \begin{array}{l} HCOOH + \; 2\,HI \\ \hline CHI_3 \quad + \; 3\,HI \end{array}$$

$$\text{or } C_2H_5OH + 8I + H_2O = CHI_3 + 5HI + HCOOH$$

Of course, in place of HI and formic acid, their Na salts are

obtained. This action is essentially an *oxidation* due to the oxidizing action of the iodine.

NOTE.—Chloroform is made in the same way, from alcohol, by means of free chlorine gas: the latter is frequently added in the form of chlorinated lime (chloride of lime).

### 16. The Determination of the Percentage of Ethyl Alcohol in a Liquid.

The determination of the per cent of alcohol in liquids containing also materials other than alcohol is accomplished by distilling the alcohol out of the liquid, determining the specific gravity of the distillate, and calculating the per cent of alcohol from the data obtained in this connection.

**Experiment.**—Secure a 200 c.c. distilling flask and a 2 ft. Liebig condenser, and mount the apparatus in the same way as shown in the figure with Art. 8 in this chapter. Hang the empty flask on a sensitive balance, weigh it and put into the flask exactly 100 grams of the liquid obtained in Art. 14. Accurately weigh a 200 c.c. flask to be used as a receiver, and distill at the rate of 2 drops per second until about 40 c.c. have been collected in the receiver. Then add enough distilled water to bring the total weight of the liquid in the receiver to 50 grams. Take the specific gravity of this liquid with a plummet and balance, and note its temperature. With this data, look up, in a table, the per cent of alcohol in the distillate, and divide this by 2 to obtain the per cent in the original sample.

### 17. Descriptive Data on Ethyl Alcohol.

Alcohol and water cannot be completely separated by distillation: at least 4 per cent of water will remain; hence the best commercial alcohol contains about 95 per cent of pure alcohol. The last traces of water can be removed by dehydrating agents only.

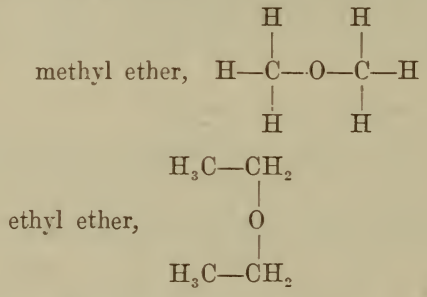
Ethyl alcohol is one of the most important substances used in industry; e. g., as a *solvent* for gums and resins in making varnishes, lacquers, etc. The amount needed for this purpose is almost inconceivably large. Since it is the least poisonous of all alcohols, its place cannot—should not—be taken by others. The cost of production of this alcohol can possibly be so low that alcohol may even be considered as a possible rival of gasoline for internal combustion engines, and as a rival of kerosene for cooking stoves and for lamps. Alcohol has a decided advantage over kerosene and gasoline because its use as a fuel is attended with less danger and it forms no soot or odor. It can be produced profitably from cheap or refuse grain, potatoes, and even from sawdust. The "Denatured Alcohol Law" passed on June 7, 1906, made it possible to put this material on the market without the payment of the enormous revenue tax. Tax-free alcohol is absolutely necessary for the development of our industries. The price at which it is obtainable at present is still about five times

as great as that at which it could be furnished. In order to stimulate the manufacture of denatured alcohol, the U. S. Bureau of Chemistry has built and operated an experimental plant, and has thus determined the cost of such a plant and its operation. The results thus secured, together with direction for denaturing alcohol and all the legal requirements to be complied with in its manufacture, have been published in Bulletin No. 130 of the Bureau of Chemistry, U. S. Department of Agriculture, entitled: "The Manufacture of Denatured Alcohol," by H. W. Wiley. This bulletin is distributed free by the government.

The object of *denaturing* alcohol is to render it unfit for drinking. The denaturant must be repugnant to the state and intolerable to the stomach—yet it should not be deadly; and it must be so difficult to remove from the alcohol that it will not pay to do it. The main formula for denaturing is: 10 parts of wood alcohol and one-half part of benzine to 100 parts of 90 per cent ethyl alcohol.

### 18. Ethyl Ether.

*Ethers* are compounds in which two carbons—one in each of two hydrocarbon radicals—are connected through an O atom—or in other words, by the two bonds of an O atom,—e. g.




Ethers are made directly from alcohols: the reaction *appears* as a dehydration merely,—e. g. $2CH_3OH=(CH_3)_2O+H_2O$.

### 19. Illustration of the Preparation of Ordinary (Ethyl) Ether or Sulphuric Ether.

Put a few c.c. of 95 per cent alcohol into a test-tube, insert a thermometer and add gradually an equal volume of concentrated sulphuric acid. Stir the mixture after each addition. Then heat it gently to 145 degrees C., and observe the odor of the vapor issuing from the test-tube. This illustrates how ether is manufactured commercially. It *appears* as though the reaction were merely a dehydration of the alcohol.

Ether, just like alcohol, is of great importance industrially—mainly as a solvent for fats, resins, etc., and also as an anesthetic. It has a very low boiling point (34.9° C.) and is very inflammable.

**20. Aldehydes.**

Aldehydes are the direct products of oxidation of alcohols. The oxygen of the oxidizer acts on the "alcohol" group as indicated in the following equations:

$$\underset{\text{methyl alcohol}}{H_3C{-}O{-}H} + O \longrightarrow \underset{\text{formaldehyde}}{H_2C{=}O} + H_2O$$

$$\underset{\text{ethyl alcohol}}{H_3C{-}C{-}O{-}H} + O \longrightarrow \underset{\text{acetaldehyde}}{H_3C{-}\overset{\displaystyle O}{\overset{\displaystyle |}{C}}{=}O} + H_2O$$

The different aldehydes are named with reference to the acids that they are changed to on further oxidation, which for the above aldehydes are formic acid and acetic acid, respectively.

Aldehydes are prepared, even commercially, by the oxidation of alcohols. For an illustration of this simple action, mix 1 c.c. of ethyl alcohol with an equal volume of dilute sulphuric acid, put into the mixture a pinch or two of powdered potassium bichromate (an oxidizing agent!) and warm the mixture: the acetaldehyde formed reveals itself by a pungent, slightly sour odor (decidedly different from that of alcohol) and the change of the color of the mixture, from red to green, shows that the chromate has been reduced.

Formaldehyde is now very important in every-day life because its vapor is a powerful poison for bacteria, but not for higher forms of life, and since it penetrates through cloth and into every crevasse, without any injurious effects to fabrics, etc., it is used to disinfect dwellings which have been infected by disease bacteria. It is obtained commercially by the oxidation of wood alcohol.

Coil some thin copper wire around a pencil, thus forming a spiral about three inches in length; hold this with the tongs in the top of a Bunsen burner flame to oxidize its surface thoroughly, and while hot drop it into a test-tube containing 1 c.c. of wood alcohol. Note the sharp odor of the formaldehyde formed.

In the commercial preparation, a mixture of wood alcohol and air are brought in contact with hot copper oxide: the copper oxide oxidizes the alcohol, and then the air oxidizes the reduced copper again. Since air alone oxidizes wood alcohol very slowly, the copper oxide acts as a "catalyzer" or hastener of the action. It is now considered that all "catalyzers" are effective through such "intermediate" reaction.

**21. The Use of Formaldehyde as a Disinfectant.**

Formaldehyde is found in commerce in the form of a 40 per cent aqueous solution, called formalin. Its wholesale price is about 10 cents a pound, and its retail price should be from 20 to 50 cents,

according to quantity. Many methods have been proposed to vaporize the formaldehyde and inject it into a room. The following are the most convenient, the "permanganate" method being slightly less troublesome than the "lime" method, but about twice as expensive:

(a) Permanganate method. For every 1000 cu. ft. of room space to be disinfected, secure 1 pint of formalin and 6½ ounces of permanganate of potash. Close tight all doors and windows of the room, spread out over chairs, etc., all bedding and other cloth material so that it will be in as thin layers as possible, open all drawers and cupboards in the room so that the gas may have access to them. Then secure a metal bucket and a large dishpan, place the pan on the floor and the bucket in it, pour the formalin into the bucket, and then pour the permanganate into the liquid in such a manner as to mix them somewhat. The generation of the gas will begin immediately. The room should remain closed for at least 4 to 8 hours. Fine polished furniture should have its flat top covered with a thin cloth to catch a small amount of dust formed by the chemicals.

(b) The lime method. For every 1000 cu. ft. of room space, secure a ½ pound of formalin and ½ pint of concentrated sulphuric acid, and 1 pound of fresh "lump" or quick lime. Place the formalin in an earthenware dish or pitcher, pour the acid into it, and allow the mixture to cool.

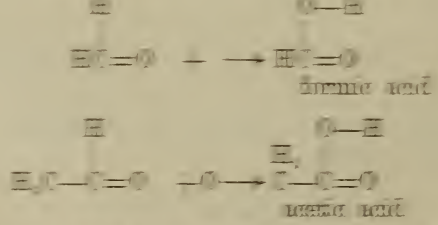
Then put the quick lime into a bucket and the bucket into a dishpan, add the formalin-acid mixture, and spread a newspaper lightly over the bucket to catch the "spatterings."

For a demonstration of the above, pour a few c.c. of formalin upon several grams of permanganate crystals.

In the permanganate method the heat evolved by the "burning" up of a part of the formaldehyde to $H_2O$ and $CO_2$ vaporizes the other part. The lime method makes use of the fact that lime takes up the water to hydrate itself, and thus leaves the formaldehyde gas without a solvent.

## 22. Organic Acids.

Oxidizing agents convert aldehydes easily into organic acids. The following equations show the formation and structure of the characteristic acid groups—




The COOH group (called "carboxyl"), with the fourth valence of the C attached to either H or another C is the essential component of all carbon acids. The simplest example is HCOOH.

formic acid; and next to this comes $CH_3COOH$, acetic acid. The "carboxyl" group may be present more than once in a molecule. The hydrogen of the COOH group is the "acid" hydrogen.

Acetic acid, which is one of the most important of these acids, is one of the products obtained in the destructive distillation of wood (see Art. 37). It is also obtained by the fermentation of dilute aqueous solutions of ethyl alcohol.

### 23. Genetic Relationship of Hydrocarbons, Alcohols, Aldehydes, and Organic Acids.

From an inspection of the foregoing articles (12, 20, and 22), it will be seen that an organic acid can be prepared from a hydrocarbon by means of the following steps:

1. $C_2H_6 + Cl_2 \longrightarrow CH_3—CH_2Cl + HCl$

   (hydrocarbon) (alkyl chloride)

2. $CH_3—CH_2—Cl + AgOH \longrightarrow CH_3CH_2—OH + AgCl$

   (alcohol)

3. $CH_3—CH_2—OH + O \longrightarrow CH_3—\overset{\overset{O}{\|}}{C}—H + H_2O$

   (aldehyde)

4. $CH_3—\overset{\overset{O}{\|}}{C}—H + O \longrightarrow CH_3—\overset{\overset{O}{\|}}{C}—OH.$

   (organic acid)

This relationship is perfectly general, and should be kept well in mind. The student will be asked to outline the scheme by which such acids as proprionic and butyric could be prepared from the proper hydrocarbons.

### 24. Esters.

A mixture of ethyl alcohol and acetic acid react slowly according to the following equation:

$$H_3C—\underset{H_3}{C}—OH + HO—\overset{\overset{O}{\|}}{C}—CH_3 \longrightarrow H_3C—\underset{H_2}{C}—O—\overset{\overset{O}{\|}}{C}—CH_3 + H_2O$$

or $C_2H_5OH + CH_3COOH = CH_3COO.C_2H_5 + H_2O$

The new compound is composed of the alcohol radical and the acid radical: it has the C in the alcohol group linked by an O atom to the C in the acid group. Compounds which contain such structures or which are thus made by the joining of alcohol and acid radicals are called esters.

### 25. Preparation of the Ethyl Ester of Acetic Acid.

Put into a test-tube 1 c.c. of ethyl alcohol and 1 c.c. of glacial acetic acid and then add cautiously 1 c.c. of concentrated sulphuric acid. Shake the mixture and warm it gently—then note the "fruity" odor. The sulphuric acid here serves merely as a catalytic agent to increase the velocity of the reaction between the alcohol and the acid.

### 26. Final Suggestions on the Foregoing Types of Compounds.

The theoretical relations pointed out above between the hydrocarbons, alcohols, ethers, aldehydes, acids, and esters, as well as the structures of their characteristic groups should be well memorized because these classes of compounds are of common occurrence and the many different members of these groups have, in general, the same properties—which are really the properties of the characteristic groups: i. e., the alcohol group, the ether group, the aldehyde group, etc. That these groups determine, to a large extent, the properties of their compounds, is true even of compounds with two different groups: the properties of such mixed compounds are in the main the sum of the properties of these groups. Hence it is seen that the study of organic chemistry pursued in the manner shown here is not nearly as laborious as the great number of different compounds possible might lead one to think.

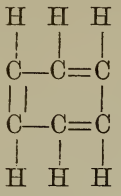
### 27. Exercise.

1. How many grams of chlorine are required to change 10 gms. of ethane into ethyl chloride? to convert 30 gms. ethylene into ethylene chloride?
2. Write the structural formulas of the following compounds: propyl aldehyde; propyl ester of acetic acid; ethyl propyl ether; ethyl chloride.
3. How would you prepare chloroform? Write the equation.

### 28. The Aromatic or Cyclic Series of Carbon Compounds.

All the compounds presented so far may be considered to be derived from the paraffin hydrocarbons, and any one of them might be prepared from any one of the others. The very large group of carbon compounds which are thus related form one of the two main divisions of organic compounds. On account of the theoretical form of the skeleton of carbon compounds, they are called the *open chain* or *straight chain compounds*. The other main division of carbon compounds are called the cyclic compounds because they always contain one or more *rings* of carbon atoms in their molecules. It should be recalled that the open chain compounds are also designated as the fatty compounds, while the cyclic compounds are designated as the aromatic compounds.

The most important carbon ring or cycle found in these "cyclic" compounds is seen in its simplest form in the compound known as *benzene or benzol,* $C_6H_6$, the theoretical structure of which is written thus:



The figure shows that every C atom is connected with *four* bonds to the other atoms—which is in accordance with one of the fundamental ideas upon which the structure of all carbon compounds is worked out.

These H's which are directly on the benzol ring are easily acted upon by reagents, and through their reactions other elements or radicals are put in place of one or more of the H's—e. g., $C_6H_5Cl$, $C_6H_5OH$, $C_6H_5CH_3$, etc. As may hence be expected there exist many compounds with a benzene ring in their molecules. This benzene ring has decided characteristic properties and it influences the properties of its compounds so largely that all compounds containing a benzene ring have many properties in common.

Besides the *one-ring nucleus* of which benzol is composed, there is a two-ring nucleus, naphthalene, $C_{10}H_8$, and two "three-ring" nuclei, $C_{14}H_{10}$, called anthracene and phenanthrene, with properties similar to benzol, and which together with their compounds are included under "aromatic" compounds.

### 29. The Commercial Source of Aromatic Compounds and Their General Properties.

The commercial source of aromatic compounds is the product obtained in the distillation of bituminous coal in the gas and coke industry. This product consists of an aqueous portion containing ammonia and of an oily portion containing the light aromatic oils and the coal tar. The oil portion is subjected to a fractional distillation and yields first a series of "light oils," which are lighter than water. It is usually known as coal-tar naphtha. It contains benzene together with some of the simplest hydrocarbon compounds. When pure, benzene distills at 80.5° C., and has a specific gravity of 0.899 at 0° C.

As the application of the heat to the tar still is continued and the lower boiling constituents distill out, the temperature rises, and higher boiling constituents pass over. When the specific gravity of the distillate has reached 1, then the receivers are changed; the temperature of the still is then from 170 to 190 degrees C.

The next fraction (called "middle oil") is composed of the distillates up to about 230 degrees C. and contains among other substances carbolic acid ($C_6H_5OH$), and naphthalene. The distillates obtained above 230 degrees C. are called "heavy oils"; they are used wholly or in part for the creosote oil of commerce—for the preservative treatment of timber. Sometimes the portion which distills above 270 degrees C. is collected separately in order to secure the solid *anthracene* which separates from it on cooling. The distillation is either arrested at a temperature between 270 and 300 degrees C., in order that the mass remaining in the still may be used as *soft pitch* (see below), or it may be carried to 340-380 degrees C. in order to secure *hard pitch*.

Properties and uses of the tar distillates: The *light oils* yield mainly benzene and some closely related hydrocarbons.

When the "middle oil" fraction cools, naphthalene separates from it in crystalline flakes, and may be separated from the oily portion by filtration, etc.

Naphthalene is a powerful germicide, and is used for disinfecting purposes, as well as for the manufacture of some dye stuffs.

The oil filtered from the naphthalene is treated with caustic soda solution to extract the carbolic acid, and the aqueous extract is then acidified (with $H_2SO_4$; see the experiment below). Thus the carbolic acid is liberated again, and since it forms a layer of oil on top of the aqueous liquid, it is readily separated from the latter. It is used either in this crude form, or after more refining. The germicidal properties are well known.

The "heavy oils" are composed mainly of chemically neutral bodies—i. e., they are neither *acidic* nor *basic*. However, they are all germicidal, a fact which has made them valuable as wood preservers, for which the hydrocarbons of the paraffin series are unsuitable because they are *not* germicidal.

All components of the coal tar oils belong to the aromatic (or cyclic) series of compounds. Hence they all—even the hydrocarbons—react readily with reagents such as nitric acid, sulphuric acid, the halogens, etc., in which reactions the H's directly on the cyclic group are attacked and replaced by other elements or radicals. This great reactivity of the cyclic hydrocarbons presents a striking contrast to the non-activity which characterizes the straight chain hydrocarbons,—that is the petroleum compounds.

Pitch is an excellent *binder*, and is used as a roofing material (spread on paper, or impregnated with sand and gravel, etc.). "Asphalt paint" is made by dissolving hard pitch in crude benzol or naphtha. The latter evaporates readily, and leaves a smooth coat of pitch. This paint is used to protect iron structures, pipes, sinks, etc. It does not last well on exposure to light and air (it "alligators"), but it does well on material that is frequently re-

painted, or which is placed in the ground, as water and gas pipes. Such tar or asphalt paint must not contain much free carbon, because the latter tends to stimulate rusting on iron. Raw tar is sometimes used to paint iron, but the ammonia, naphthalene, and possibly other substances present tend to corrode iron, and hence the use of raw tar is inadvisable.

### 30. Tar Oil for the Preservation of Timber.

The preservative treatment of timber is effected either by injecting a large quantity of an antiseptic liquid into the wood under pressure or by dipping the wood so as to allow the surface to absorb such a liquid. The liquid required for the second procedure must naturally be one which withstands exposure to heat and rain perfectly: hence it should be composed of insoluble oils boiling above 270 degrees C. In neither treatment is it intended to form a protective coating or to attempt to exclude moisture: moisture can enter or leave such timbers freely, but contact with these fungicidal oils renders it sterile, and thus inhibits the growth of wood-decaying fungi.

A great many steam railroad ties are impregnated under pressure with a solution of zinc chloride. This salt is a fungicide, and preserves ties fairly well in dry countries, though not for as long a time as creosote.

*Creosote* is an indefinite term which designates vaguely an oil used for wood preservation: it may be anything from the volatile portion of the tar distillates, which would soon evaporate on exposure, to the valuable, permanent high boiling oils. In buying and selling creosote, its quality should be defined by a specification,—or better still, the term creosote oil should be dropped and the term tar oils should be substituted because everybody would realize immediately that the term is indefinite.

It was formerly assumed that the preservative power of the heavy tar oils—creosote—was due to the tar acids and to the naphthalene in it and that certain amounts of these were required to be present in oils used for wood preserving, but recent analysis of well preserved timbers that have been in service for various lengths of time have revealed that the tar acids and naphthalene disappear from preserved timbers fairly soon after treatment (tar acids, by dissolution in water; naphthalene, by evaporation), while the higher boiling oils (particularly those which distill above 270 degrees C.) remain in the timber and preserve it. In explanation of this action of the high boiling oils it should be stated these oils are practically insoluble in water, non-volatile, and yet strongly germicidal. Hence modern specifications call for as low a per cent of tar acids and naphthalene and as high a per cent of high boiling oils as possible.

### 31. The Production of Wood Preserving Oil.

Practically all the coke made for use in the production of iron from its ore is prepared in such a way that the tar is saved; and the latter is distilled until the residue forms hard pitch. Hence this industry can furnish an excellent creosote—one containing a large amount of high boiling tar oils.

### 32. Tar Oils: The World's Great Germicides.

Tar oils are largely used as fungicides and germicides, not only in the original state—e. g., as crude carbolic acid, and solid naphthalene, for the disinfection of cesspools, abattoirs, etc.—but also in the form of an aqueous solution. Tar oils dissolve readily in water which contains a sufficient amount of soap. Many proprietary disinfectants, such as "Cresol," "Chloro-Naptholeum" and similar substances with fanciful names are merely soap solutions of tar oil or of "crude" carbolic acid.

For disinfection, these aqueous solutions may be poured or sprinkled into sinks and drains in the original concentrated form, or they may first be diluted with water. In the latter case the oil will separate extensively out of solution, but the milk-like emulsion contains the oil in the form of very small globules. This serves also as an insecticide, in chicken yards, for exterminating flies, etc.

Either the aqueous solution or the creosote oil may be added to sawdust to produce an effective germicidal "sweeping" compound. The commercial sweeping compounds are generally made from the non-germicidal petroleum oils, although these are not as suitable for this purpose.

### 33. Experiments With Tar Oils.

Set up the same distilling apparatus that was used for the distillation of crude petroleum. Put about 150 c.c. of "creosote for pressure treatment of timber" or crude carbolic acid into the distilling flask, and proceed to distill this as you distilled the crude petroleum. When the thermometer indicates 195 degrees C., put a clean receiving flask on the end of the condensing tube and collect the next 30 c.c. (approximately). Note the final temperature and put another clean receiving flask on the condensing tube and collect about 70 c.c. of the next distillate. Again note the final temperature. The first 30 c.c. will contain a great deal of the carbolic acid in the sample, and will be used to show the extraction of this acid, while the 70 c.c. sample will serve as a fair representative of ordinary heavy oil (creosote) with which some of its properties and uses may be shown.

### 34. The Extraction of Carbolic Acid.

To the 30 c.c. distillate obtained above add 20 c.c. of a 20 per cent sodium hydroxide solution, stir the mixture vigorously and heat it to the boiling point; then allow it to cool. By means of a large dropping funnel separate the aqueous from the oily layer. Add another 10 c.c. of sodium hydroxide solution to this oil, stir and heat the mixture and separate it again. Then throw away the oily residue.

Pour the caustic soda extract into a 250 c.c. flask, allow it to cool, add

dilute sulphuric acid to it slowly and shake the mixture thoroughly after each adidtion, and continue the addition of the acid until the mixture reacts acid to litmus. Then add water until the flask is filled well into the neck. Note that an oily layer will collect in the neck of the flask. Observe its odor. By what chemical reactions was it separated from the oil and liberated again?

**35. Demonstration of Some Properties of Tar Oils.**

Take the 70 c.c. distillate obtained above, cool it to the temperature of the tap water by allowing the latter to run on the outside of the flask and determine the specific gravity of the oil with the specific gravity balance. Note the temperature of the oil while the specific gravity is being measured. In recording this result, state the temperature between which this sample was obtained on distillation and also the temperature at which the specific gravity was taken. Compare these data with the corresponding data on petroleum oils:—the specific gravities of coal tar fractions obtained above 200 degrees C. are always greater than 1.0, while the specific gravities of all petroleum distillates are less 1.0. This fact is used by chemists to ascertain whether or not wood preserving oils are pure tar oils or have been adulterated with crude petroleum.

To contrast the great reactivity of tar oil with the non-activity of petroleum oils, put some 20 c.c. of this 70 c.c. sample into a separate small flask and put about 20 c.c. of regular petroleum oil into another flask.

Add four to five times as much concentrated sulphuric acid to each oil, stir the mixtures vigorously and heat them gradually to about 60 degrees, then set them aside for about one-half hour, shaking them at intervals. Next take two large flasks, fill them one-half full of tap water and then pour one of these mixtures gradually into one flask, and the other into the second flask. Finally fill both flasks with water well into the neck and allow them to stand undisturbed for several hours. In the flask containing the petroleum oil almost the whole of the original sample will reappear in the neck, while in the other flask practically none of the tar oil will appear, which shows that the petroleum oils are very slightly attacked by the concentrated sulphuric acid, while the tar oils are completely attacked and converted into water-soluble compounds.

**36. The Preparation of Tar Oil Disinfectants and Germicides.**

Cut about 25 grams of rosin soap into fine shavings, add an equal weight of distilled water, and warm and stir the mixture until the soap has been dissolved. Then add an equal volume of crude tar oil, heat and stir the mixture: a solution of the appearance of black coffee will be obtained.

This solution was referred to in the descriptive matter above. It has great germicidal power and is found in the trade under such names as chloro-naphtholeum, creoline, etc.

Mix some of this black solution with about fifty times its volume of water:—the mixture will become milk white, will clear up on standing and it will then be found that the tar oil has settled out to the bottom. The surface forces of this dilute soap solution are not able to "dissolve" the oil—hence it separates, at first in very small globules, which give the mixture the milk white appearance.

**37. Chemical Products Made by Distillation from Wood and Resins.**

To complete the list of chemical manufactures based on the distillation of raw materials, mention should be made of the manufacture of turpentine, rosin, rosin oil, charcoal, wood alcohol,

acetic acid, and acetone,—all of which are commercially extremely important and all of which are obtained from wood as the raw material.

The resins obtained by "bleeding" or "boxing" resinous pine and fir trees are mixed with water and the mixture is distilled: the distillate contains a mixture of oils which is commercially known as "gum" turpentine, and the simplest representative of which has the formula $C_{10}H_{16}$. These oils are evidently unsaturated hydrocarbons. The residue left in the retort is the rosin or colophony of commerce.

When rosin is subjected to further dry distillation, it yields a distillate called rosin oil, which is used to make axle grease, and it is also used as a cheap (worthless) substitute for linseed oil in paints.

The destructive distillation of non-resinous wood yields the following products:

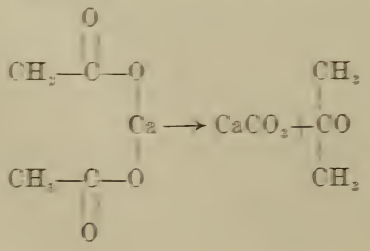
(a) An aqueous distillate called pyroligenous acid, which contains, among other ingredients, acetic acid and wood alcohol.

(b) Wood tar, for which there is very little special use, and which is used for fuel mostly.

(c) Charcoal, which remains as a residue in the retort.

If the wood is resinous, it is first mixed with water and then subjected to distillation. The large amount of steam first distilled carries with it the turpentine from the resin in the wood: and this portion of the distillate is collected separately. The subsequent "dry" distillation of this wood yields about the same products as the distillation of the nonresinous wood just described above. The turpentine obtained in this distillation is called *wood turpentine:* it has a higher boiling point than the gum turpentine, but is chemically quite similar to the latter.

Distillate (a), the pyroligenous acid, has the acid in it neutralized with lime, then the wood alcohol is distilled out of it, and finally the water is evaporated to obtain dry acetate of lime. The latter is used largely to make acetic acid (by treatment with sulphuric acid and distillation); calcium acetate is also distilled dry, under which condition it yields a distillate of acetone $(CH_3)_2CO$, a commercially important liquid, which is formed according to the following equation:



**Questions on Chapter XIII.**

1. Figure out as shown in Art. 2 how many different compounds with the formula $C_6H_{14}$ are theoretically possible.

2. Give two different names for the compound of the formula $CH_3Cl$, and give the complete equation for its formation by the interaction of chlorine and methane. If $CCl_4$ is made by the action of chlorine on methane, then how many grams of HCl are produced while one gram of $CCl_4$ is produced?

3. One gram of ethylene, $C_2H_4$, is converted to the corresponding saturated compound by treatment with chlorine gas. Calculate how many grams of the resulting product are obtained.

4. State exactly what is meant by a crude oil having a paraffin base, or having an asphalt base. How is the binding power of asphalt or crude oil residue used for road building "measured?" By what measurements are lubricating oils measured? How is praffin manufactured: state exactly. Why is sulphur objectionable in gasoline or kerosene: explain the chemical action that takes place in the removal of sulphur from such oils? If you were looking for a material with which to paint table tops, etc., in order to protect them against the action of chemicals, would you take a varnish, the chief constituent of which is a resin similar to rosin in chemical property, or would you take an oil like linseed oil, or would you choose some other fatty or waxy material: state which and why?

5. Draw all the structural possibilities for an alcohol of the composition $C_3H_7OH$.

6. Give the structural formula of propyl ether and state with which substances and what operations it would be produced.

7. Give the structural formula of the propyl ester of propionic acid and state from what substance and what operation it would be produced.

8. How is the disinfectant known as cresol made? What is creosote: define the characteristic of a first-class quality of creosote. Why do tar oils preserve wood? What is the formula of carbolid acid? of sodium carbonate? Write the reaction which takes place in the extraction of carbolic acid from tar distillates by means of caustic soda solutions.

9. What is rosin oil? For what is it frequently substituted?

## CHAPTER XIV.

## APPLIED ORGANIC CHEMISTRY: ANIMAL AND VEGETABLE FATS AND OILS, CARBOHYDRATES, AND NITROGENOUS FOOD CONSTITUENTS.

### 1. Properties and Uses of Some Important Oils of Animal and Vegetable Origin.

The vegtable and the animal fats and oils have the same general composition: they are mixtures of glycerin esters of several "straight-chain" carbon acids. The fatty acids which make up the greater part of these fats have from 16 to 18 C's to the molecule, and only one carboxyl (COOH) group. Glycerin is a trihydroxyl alcohol, $C_3H_5(OH)_3$, hence it reacts with three molecules of the "fatty" acids according to the following equation:

$$3\ RCOOH + C_3H_5(OH)_3 = C_3H_5(RCOO)_3 + 3\ H_2O$$

Here R represents the rest of the acid molecule except COOH, and is a hydrocarbon radical. The formula $C_3H_5(RCOO)_3$ expresses the composition of all fats and oils of animal and vegetable origin.

Glycerides of the following acids are found as components of fats and oils.

*Saturated acids:*

Butyric acid, $C_3H_7COOH$
Lauric acid, $C_{11}H_{23}COOH$
Palmitic acid, $C_{15}H_{31}COOH$
Stearic acid, $C_{17}H_{35}COOH$

*Unsaturated acids:* In all of the following unsaturated acids the hydrocarbon radical contains 17 C, hence if they were saturated the hydrocarbon radical in each one would contain 35 H, as in stearic acid above; the number of H which they have *less than 35* indicates the amount of unsaturation in the acid molecule—

Oleic acid, $C_{17}H_{33}COOH$, amount of unsaturation, 2H, or one double bond.

Linoleic acid, $C_{17}H_{31}COOH$, amount of unsaturation, 4H, or two double bonds.

Linoleinic acid, $C_{17}H_{29}COOH$, amount of unsaturation, 6H, or three double bonds.

The glycerides of palmitic acid (palmitin) and of stearic acids (stearin) are white crystalline solids, melting at 61 and 72 degrees C., respectively: that of oleic acid (olein) melts at 14 degrees C., and hence is liquid at ordinary temperatures, and the glycerides of linoleic and of linoleinic acids have probably still

lower melting points. The solid fats are composed in large part of stearin or of palmitin or of both, while the liquid oils are composed largely of olein, linolein, etc.

Fresh fats and oils are nearly odorless and neutral in reaction, but when exposed to the air small portions are frequently "hydrolyzed" by the moisture of the atmosphere, and thus a small amount of the free fatty acids and of glycerin are formed. This action is usually *induced* by the fermentation or putrefaction of substances of a gelatinous or albuminous nature which are always present in raw fats and oils, and is accompanied by numerous secondary reactions which produce small amounts of bodies of disagreeable odor and taste. The oil is then said to be rancid. In "refining" vegetable oils; e. g., cotton seed oil, the albuminous bodies are removed and hence the refined oil does not become rancid as readily as unrefined oil.

The fats and oils are specifically lighter than water. They cannot be boiled or distilled, even under *reduced* pressure; heated much above their melting point, they *decompose* into various substances.

The glycerides of the unsaturated acids—particularly those of linoleic and linoleinic acids—take up rapidly, or react energetically with, oxygen, iodine, sulphuric acid, etc. The substances combine with the oil molecules at the double or triple bond, just as HCl combines with ethylene, $CH_2CH_2$ to form $CH_3CH_2Cl$, and bromine combines with acetylene to form $CHBr_2CHBr_2$. When oxygen combines with such glycerides at the point of "unsaturation," thick, gummy or resinous masses are formed, which in thin layers become hard, dry, transparent or translucent films, and the change is hence commonly called "drying"—e. g., as in the *drying* of oil paints, etc.

### 2. The Manufacture and Properties of Cotton Seed Oil.

Cotton seed oil is a mixture of glycerides of fatty acids in which the liquid glycerides (e. g., olein) predominate. It contains approximately 22 to 31 per cent of saturated compounds (mostly palmitin with a little stearin), 59 to 52 per cent of olein (one double bond in each acid radical), and 19 to 16 per cent of linolein (two double bonds in each acid radical). The glyceride of linoleinic acid (with three double bonds in the acid radical) is practically absent. On account of the absence of the last named glyceride and the predominance of the *slightly* unsaturated olein, cotton seed oil does not dry to a film as linseed oil does (see below), yet it becomes viscous when it is oxidized (by the air).

*The manufacture of cotton seed oil:* Fresh cotton seed is cleaned by passing it first through a screen with a mesh slightly larger than the seed, and then over a screen with a mesh slightly smaller than the seed: thus, objects both larger and smaller than

the seed are removed. It is then *"re-ginned"* to remove the lint, and then *de-hulled*. Finally the meats are crushed between rollers.

The per cent of the different substances thus obtained from the seed are as follows: Hulls, 48.9 per cent; linters, 1.1 per cent; crushed meats, 50 per cent. The latter yields about one-fourth *oil* and three-fourths meal.

To prepare the cotton seed meats for the press, the meats are first cooked. The purpose of this is to modify the consistency of the meats through heat so that the oil may be expressed as completely as possible. The heat also expels the excess of moisture and coagulates the albumen. The cooked meats are then molded into cakes to fit the press, and finally the oil is pressed out by means of hydraulic pressure. The cakes taken out of the press are then ground up into the cotton seed meal, which is a valuable feedstuff.

The crude oil is reddish brown in color, and contains impurities. These ferment or putrefy readily and induce the liberation of free fatty acids and other products which make the oil rancid. The amount of free fatty acid in oil is hence an indication of its age, and in commerce its determination is frequently required. Since with the removal of the impurities the tendency for the oil to become rancid becomes much less, this *refining* is undertaken as early as possible. In this operation a certain—variable—amount of oil is lost together with the impurities; hence the value of the crude oil depends on the "refining loss." The determination of the amount of this loss in any particular lot of oil is shown below.

After refining, the oil must be thoroughly dried, first by warming and then by adding plaster of Paris to the oil. This takes up the water as "water of crystallization," forming $CaSO_4$, $2H_2O$. The result is "summer yellow oil."

The yellow oil is bleached by means of fuller's earth: the finely powdered earth is stirred into the oil, and the latter warmed gently. Then the oil is filtered. This gives "summer white oil."

The summer white oil is then chilled and the solid palmitin and stearin (known as cotton seed stearin) separated from the oil by filtration. The clear light-colored oil (known as "winter oil") is extensively used as a salad oil. Except for a slight difference in flavor, it can be used, in cooking, for everything that olive oil can be used for, and it is even more completely digested than olive oil. (The digestion coefficient of cotton oil is 93.5 per cent, while that of olive oil is only 89 per cent.)

### 3. Products of Cottonseed Oil: Lard Compound, Hardened Cottonseed Oil, Oleomargarine, Etc.

Just as a solid and an oily portion may be obtained from the cotton seed oil, so they may be obtained from beef fat (tallow). These products of tallow are known as oleo-stearin and oleo-oil, respectively. "Lard compounds" are mixtures of "summer white"

cotton seed oil (which contains all its stearin, etc.) and oleo-stearin. Sometimes hard stearin is used in place of oleo-stearin. Lard-stearin is manufactured from lard just as oleo-stearin is obtained from tallow. Lard compound is made chiefly by the packing houses, as it is a convenient and profitable way to dispose of their large amounts of beef tallow obtained in the slaughtering of cattle.

Hardened cotton seed oil is now being manufactured in large quantities in the United States. Cotton seed oil consists principally of olein (the glycerine ester of oleic acid); oleic acid is an unsaturated acid, as an inspection of the formula, $C_{17}H_{33}COOH$, will reveal. The amount of unsaturation is 2 (i. e., the molecule of oleic acid is capable of taking up 2 additional hydrogens). If these two hydrogens are actually taken up by the molecule of oleic acid, it is changed from oleic acid to stearic acid, $C_{17}H_{35}COOH$, which is a saturated acid. The glycerine ester of stearic acid is a solid at room temperatures and somewhat above. Thus, the process of hardening cotton seed oil is one of *hydrogenation;* the process consists simply in the adding on of six hydrogens to the molecule of olein, two hydrogens for each molecule of oleic acid in the molecule of olein. The patents covering the process are patents governing the method by which the hydrogen (in the form of gas) is caused to add on. "Crisco" and "Crusto" are examples of the many trade names under which this hardened cotton seed oil is put on the market for consumption.

Peanut oil is similarly hardened, and also produces a nice, firm white "lard." Representative of this type is the trade article "Pindapan."

Cotton seed oil is also used in making oleomargarine. One formula for making this butter substitute runs as follows:

| | |
|---|---|
| Oleo oil | 495 pounds |
| Lard | 265 pounds |
| Cotton seed oil (summer yellow) | 315 pounds |
| Milk | 255 pounds |
| Salt | 120 pounds |
| Color | 1¼ pounds |

These substances are merely mixed mechanically.

Cotton seed oil, particularly those grades which have undesirable flavors or colors, are used to make soap.

#### 4. Methods for the Determination of the Amount of Oil in Cotton Seed and Cotton Seed Meal.

At present cotton seed is bought and sold blindly—without any consideration of the quantity and quality of the oil contained in it. The following directions show that determinations suitable for the trade may be made without difficulty even by people who have had but little chemical training. By means of such analyses the buy-

ing and selling of cotton seed could be made much more rational than it now is.

### 5. Determination of the Per Cent. of Oil in Cotton Seed—Harry's Method.

In this experiment the non-combustible carbon tetrachloride is used where either ether or petrolic ether, is employed by chemists. The use of carbon tetrachloride makes the operation perfectly safe, while ether makes the operation very dangerous.

Secure about 120 c.c. carbon tetrachloride, and determine its specific gravity, at a definite, known temperature with a pycnometer or with a specific gravity balance. For this purpose the capacity of the pycnometer should have been determined previously, or should be determined to begin with. To determine the specific gravity of the carbon tetrachloride, fill either a pycnometer or the cylinder belonging to the specific gravity balance with this substance and place the filled vessel into a large beaker filled with tap water and allow it to remain there until the oil and the water may have equalized their temperatures. Measure and note the final temperature carefully. Then, if the balance is being used, weigh the plummer while the cylinder remains in the water; if the pycnometer is being used, secure a short piece of ordinary glass tubing and make out of it a small pipette with a capillary end, and by means of this fill or empty the pycnometer to the bolting mark, then take it out of the water, wipe it dry, weigh it, and calculate the specific gravity of the carbon tetrachloride at the observed temperature. The specific gravity at any other temperature may be obtained by *adding* 0.0016 for every 1 degree C. if this *other temperature is below the observed temperature* (or subtracting for every degree above.

Next measure out exactly 100 c.c. of carbon tetrachloride. Then weigh out, in a 200 c.c. Erlenmeyer flask, the samples to be analyzed (i. e., either 40 grams of cotton seed meal or 40 grams of seed previously chopped fine, etc.), warm it in a vessel full of water at approximately 60 degrees C. and then pour the carbon tetrachloride through a funnel upon the sample. Cork the flask loosely and place it again in the water bath and keep it in there for at least fifteen minutes. Remove it several times to shake it. Then allow it to cool, strain the contents through a cheese cloth, squeezing the sample to remove the liquid as thoroughly as possible. Then determine the specific gravity of the carbon tetrachloride oil mixture. Note the temperature. This determination need not be made at the same temperature as that at which the determination with the pure solvent was made. The specific gravity of this extract will be less than that of the solvent alone, because the cotton seed oil has a lesser specific gravity.

Calculate what the specific gravity of the pure solvent would be at the temperature at which the specific gravity of the extract was determined. From this subtract the specific gravity of the extract, divide the difference by 0.00286. The result is the per cent of oil (if 40 grams of sample were taken).

Re-distill the extract in order to separate the carbon tetrachloride from the oil. For this purpose secure a water-cooled glass condenser, a 250 c.c. distilling flask and a vessel to be used as a water bath. Carbon tetrachloride boils at 75.7 degrees C. Return all the carbon tetrachloride to the store room. As a substitute for the water-cooled condenser a glass tube five feet long may be used as an air condenser.

### 6. Demonstration of the Refining of Cotton Seed Oil.

The refining of cotton oil has for its object the removal of any free fatty acids that may have been formed (by the action of moisture and ferments) and of the albuminous matter introduced from the seed. It is accomplished by converting the free acids and a little of the oil *into soap*. As the little globules of soap, which are at first spread uniformly throughout the oil,—as they collect and form larger particles and finally settle to the bottom, the mucilaginous impurities are drawn along and collected with them.

Secure 5 c.c. of a 10 per cent solution of sodium hydroxide, and also 75 c.c. of raw cotton oil. Put the oil into a small flask or bottle and while shaking the oil, gently but constantly, add the sodium hydroxide solution in portions of a few drops at a time. Then warm the mixture by placing the flask in hot water but do not allow it to become so hot that it cannot be held against the skin; continue to stir until the mixture shows a tendency to clarify by the settling out of the soap stock. Allow the latter to settle out thoroughly, decant the clear oil and preserve it for the next operation.

### 7. Demonstration of the Bleaching of Cotton Seed Oil.

To the refined oil prepared above add approximately three to ten grams of finely powdered fuller's earth. Stir and warm the mixture in hot water and filter it through a dry filter paper. The oil should have become much paler,—if not, the operation should be repeated and possibly a larger quantity of fuller's earth should be used. The action of the fuller's earth is due purely to surface forces.

### 8. Separation of the Cotton Oil Stearin.

Put into a test-tube some of the bleached oil just obtained and cool it in ice water until its temperature is practically at 0 degree C.: those components of the oil which have high melting points will solidify and may be removed by filtration. This solid portion is mostly *palmitin*.

### 9. The Manufacture of Soap.

The soap stock—fatty material—required for soap making varies according to the kind of soap desired. For white, hard soaps, the best grades of tallow, palm oil, or cocoanut oils are used. Cotton seed oil mixed with tallow or lard also makes an excellent soap stock for white hard soap. A soap stock for hard soaps must contain a large proportion of the non-drying oils (stearin, palmitin, etc.); the sodium salts of these acids are hard, while the sodium salts of drying oils (olein, etc.), are soft like butter, and hence the latter must not be present in too large a proportion in the stock for hard soap.

A good soap should be free of disagreeable odors, free from uncombined caustic soda and also free from uncombined fat; it should be uniform in texture, and should not contain a noticeable

amount of foreign substances (filler!). A pure white color also is an indication of good quality.

Perfumes, colors and other materials added to soap as in medicated soaps seldom add anything to the value of the soap, and frequently they are added merely to mislead the public into buying an inferior article or to pay an unnecessarily high price. . Pure, good soap is a staple article that can be had at a very low price if bought of the proper source.

Hard soaps are made invariably by means of *soda,* and by "salting" the soap out of the reaction mixture—thus removing the glycerin and other—accidental—by-products. The method of preparation is demonstrated below.

In the manufacture of soft soaps, the soap stock is selected so as to contain mostly glycerides of unsaturated acids; e. g., linseed oil, cotton seed oil, etc. Furthermore, these soft soaps are made either by means of *potash,* or, if made with soda, they are not "salted" out, so that they contain the glycerin, etc.

Soap for different purposes and saponaceous compounds, such as pearline, sapolio, etc., are composed of the following substances:

*Soft soaps.*—Potash soap, together with the whole reaction mixture; i. e., glycerine and water.

*Filled or padded soap.*—Soda soap with the whole reaction mixture and frequently also impalpable earth powders or water glass (sodium silicate).

*Pure, white, hard soaps of best quality.*—Nothing but *soap* material carefully prepared so as not to contain an excess of alkali or of free fat (by repeated boiling, with careful adjustment of "stock" to lye.) It is heavier than water, but by stirring air into it, it can be made to float on water.

*Laundry soap.*—Contains, besides soap, an excess of alkali, which is desirable for laundry purposes, but to be avoided for toilet purposes. The excess of lye is incorporated in the soap by deliberate manipulation.

*Yellow soaps.*—All yellow soaps are made by using rosin for a part of the soap stock.

*Toilet soaps.*—(a) Pure, white soap of best quality (see above) is best for a toilet soap. A not undesirable addition is that of some *free oil* or vaseline to the soap: this makes the soap "lather" well.

(b) Medicated or scented soaps are merely ordinary soaps with the drugs or perfumes mechanically incorporated.

(c) Transparent soaps: These are prepared without heating the reaction mixture. This is possible by the use of a readily reacting soap stock—such as castor oil—or by the use of alcohol as a solvent for the fat. The soap contains all the

reacting mixture, and usually an extra amount of glycerine is added. The transparency is due to the presence of the glycerin.

(d) Liquid soaps: These are merely dilute aqueous solutions of soap.

*Soap powders, sapolio, etc.*—These contain gritty earthy substances bound together with a small amount of soap. They usually contain an excess of free alkali.

### 10. The Preparation of Hard Soap.

Secure about 35 grams of tallow and 15 grams of "summer oil" and 7 grams of caustic soda. Dissolve the latter in 35 c.c. of water: then take one-fourth of this and dilute it to 25 c.c. and put it into a medium-sized beaker. Melt the fat by warming it gently in a small dish, and pour it into the beaker containing the 25 c.c. of dilute solution. Heat and stir this mixture until it is thoroughly mixed, then add gradually the rest of the caustic soda (the concentrated solution), and continue to heat it, with gentle stirring, until a sample clinging to the stirring rod feels dry and firm between the fingers. About 40 c.c. of strong salt solution (25 per cent) is then to be stirred into the mixture to "salt out" the soap. The contents now should divide themselves into two layers, the upper consisting of soap paste (with water) and the lower consisting of the aqueous solutions of the salts and glycerin.

### 11. The Determination of the Main Constituents of Soap.

The following exercise is intended to enable students to find out for themselves the chief components of ordinary soap and soap powders, etc.; it is also intended as an illustration of how such work is done. However, students should not mislead themselves into believing that these directions suffice to determine all components, nor to believe that these exercises can make expert analysts out of elementary students:—the exercises merely show something of the methods which a chemist employs in making analyses of such substances as soap.

In this exercise the following components are to be determined:

(a) Insoluble matter,—sand, clay, etc.
(b) Total soap stock (sodium salts of fatty acids).
(c) Free alkali.

The amount of *water,* of *undecomposed fat,* and of *glycerin* which may be present are ignored in these determinations. In most commercial soaps, free fat and glycerin are practically absent.

(a) *Insoluble Matter:* The sample to be used should be reduced to fine shavings or to a fine powder. Weigh out in a 250 c.c. flask 10 grams of any white laundry soap or 10 grams of "Lava" soap. Add 50 c.c. or more of hot distilled water and digest the mass over a mild source of heat until the soap stock seems to have dissolved. If an insoluble residue remains, *decant* the liquid into a beaker, treat the residue with another, smaller portion of hot water, and if necessary treat it with a third portion of water. Of course the different portions of water are all col-

lected together. The residue, when free from soap stock, is washed into a weighed four-inch dish, the wash water is decanted as completely as possible and the dish and contents are dried by heating them gently over an asbestos board. Weigh the dish and contents and calculate the per cent of insoluble matter in the soap.

(b) *Total Soap Stock:* To determine (b) above, add to the aqueous soap solution exactly 40 c.c. of normal sulphuric acid from a burette, and heat the mixture nearly to the boiling point. Test it with litmus: it should contain an excess of acid, and, if necessary, more normal sulphuric acid must be added from the burette. Note the amount added.

The oily layer formed is the free fatty acid obtained from the "real" soap according to the equation:—

$$2RCOONa + H_2SO_4 = 2RCOOH + Na_2SO_4$$

The free fatty acids are evidently insoluble in water.

Secure a large dropping funnel—preferably one with an open top—and decant the oily layer into it without spilling any portion of the liquid. When the funnel is full, the aqueous layer is drawn off below and returned to the main portion. By repeating the manipulation, all of the oily layer may be transferred to the funnel. The last drops of the aqueous solution are removed from the funnel by washing with a small amount of water. Some alcohol is then put into the dropping funnel to dissolve the oil, the alcoholic solution is poured into a beaker and the funnel is rinsed out with a little more alcohol, which is added to the other alcoholic solution. A drop of phenolphthalein is added and the mixture is titrated with normal sodium hydroxide.

The number of c.c. of normal sodium hydroxide required by the alcoholic solution is multiplied by 0.306 and the result is the weight of the real soap in the original sample. Calculate the per cent of soap in the sample.

This numerical relation is obtained as follows: one mol. of acid reacts with one mol. of sodium hydroxide, hence the substances are in the ratio—

$$C_{17}H_{33}COONa : NaOH :: 305 : 40$$

(The molecular weight of sodium oleate is 305, that of sodium stearate is 307, hence in our calculation the average value of 306 is used). But 1 c.c. of normal sodium hydroxide solution contains 0.04 gram of solid sodium hydroxide, and this amount forms, by reaction, 0.306 gram of soap, as is shown by the above proportion.

(c) *Free Alkali:* Add a drop of phenolphthalein to the aqueous liquid from which the oil was separated, and titrate this also with normal sodium hydroxide. This determines the *excess* of sulphuric acid used: add the number of c.c. of sodium hydroxide here used together with the number used for the oily layer, and subtract this sum from the total number of c.c. of normal sulphuric acid added to the aqueous liquid: the remainder is the amount of acid used up by *free alkali* present in the soap. Multiply this remainder by 0.04 to obtain the weight of sodium hydroxide in the soap; then calculate the per cent of the latter present in the soap.

### 12. The Manufacture and Properties of Linseed Oil.

Linseed oil is obtained from the seeds of the flax plant. When the plants are used for their fiber, they are pulled before the seeds

are ripe, and hence the latter, before they are pressed, must be allowed to ripen after being gathered. The seed which has ripened in the fields yields the best oil.

The seeds may be pressed cold or hot, or first cold and then again hot. Cold-pressed oil is pale and tasteless, and is used for cooking in Russia. The hot-pressed oil is amber colored or dark yellow.

Linseed oil is the most important of the "drying" oils. It contains a few per cent only of the glycerides of saturated acids (palmitin, etc.), and the remainder is made up approximately as follows: 5 per cent of olein (one double bond in the acid radical), 15 per cent of linolein (two double bonds in the acid radical) and about 80 per cent of glycerides of acids, the unsaturation of which is equal to three double bonds in each acid radical. It is seen that linseed oil is composed almost entirely of glycerides of highly unsaturated acids which take up oxygen, iodine, etc., readily at the double or triple bonds in the molecules. With the progress of the absorption of oxygen, linseed oil becomes thick, and *in thin films,* changes finally to a dry, hard substance. This change naturally takes place more rapidly at higher temperatures, and hence by "boiling" the oil, and blowing or "stirring in" air during the boiling, it is largely "oxidized," so that such "boiled oil" (frequently called "hard oil") when it is spread out on a surface in a thin film requires only a short time to "dry." The boiling may be carried on to various extents: thus ordinary "boiled oil" for painting is obtained by "boiling" the oil until it has lost from 8 to 10 per cent of its weight, during which operation its temperature will rise gradually from 130 to 200 degrees C. approximately: or it may be "boiled" until the temperature rises to 260 degrees and even higher. The extent of boiling is determined by the use for which the product is to be used—e. g., as a varnish, or for printers' ink (with lamp black or other pigments), or to make oil cloth or linoleum.

Precaution: Linseed oil spread in thin films reacts so rapidly with oxygen and this reaction gives out so much heat that rags and paper which have been used to clean up paint spots, etc., frequently are ignited from this heat, and, if thrown around promiscuously, may start disastrous fires.

This reaction of linseed oil with oxygen is catalyzed enormously by small amounts of lead or manganese compounds dissolved in the oil. Dilute solutions of lead or manganese rosinate or borate in linseed oil are called *japans* or *driers,* and when small amounts of one of these is added to raw linseed oil, then films of the latter will "dry" in about twenty-four hours or so, when films of raw linseed oil without a "drier" will require about three days. Hence a "drier" is added to all paints. This catalyzing influence of lead or manganese compounds is made use of in preparing boiled oil:

when a small amount of lead oxide or resinate is added to the oil it need not be heated to so high a temperature to oxidize it rapidly, and hence a lighter colored product is obtained.

Since linseed oil commands a higher price than many other oils, and since no other oil is as well suited as a "pigment binder" in paints, it becomes necessary to test the oil used in paints. For this purpose the determinations of the Maumené number and of the iodine absorption number are best suited because the reactions in these tests involve only the double or triple bonds in the unsaturated acids, and hence "measure" the extent to which the sample has the property of "drying"—which is the *valuable* property of linseed oil.

In the examination of a supposed linseed oil, the specific gravity should also be taken. It is true that different samples of true linseed oil may show considerable variation in the specific gravity and that the other oils, such as cotton seed oil, etc., have so nearly the same specific gravity that an admixture of the latter to linseed oil would not be detected. yet with the addition of some other oil, such as rosin oil, which has a considerably different specific gravity, the specific gravity determination reveals the adulteration so readily that it always is advisable to make this test.

### 13. The Maumene Test.

The Maumené number of an oil is the *number of centigrade degrees rise in temperature caused by mixing* 10 *c.c. of concentrated sulphuric acid with* 50 *grams of the oil.* This determination would be quite accurate and fixed if the concentrated sulphuric acid would always be of the same strength of concentration. Unfortunately, "concentrated" sulphuric acid does not always contain the same amount of water; hence, in order to eliminate the errors due to a variation in this per cent of water, a further determination is made, using the same amount of acid but substituting 50 grams of water for the oil. The rise in temperature of the oil mixture divided by the rise in temperature of the water mixture gives a number which is not subject to the same variation as the true Maumené number. This number multiplied by 100 is known as the *Maumené Specific Temperature Reaction* and is by far the more reliable determination of the two. The table in Art. 16 presents both the Maumené number and the Maumené specific temperature reaction for comparison.

To make a test, weigh out in a beaker of approximately 150 c.c. capacity, 50 grams of an oil such as cotton seed oil, or 25 grams of an oil such as linseed oil. Add to the latter 25 grams of kerosene, so that all samples have the same volume. The smaller amount of an oil such as linseed oil is necessary on account of the greater extent of reaction, of the highly unsaturated oils, with sulphuric acid. Surround the beaker loosely with cotton batting and place it inside of a larger beaker, into which it should fit fairly well. Observe the temperature of the oil. Then

add gradually from a burette 10 c.c. of concentrated sulphuric acid, and at the same time stir the mixture thoroughly with the thermometer. Continue to stir as long as the temperature rises, and note the highest point at which the thermometer remains constant for any appreciable length of time. The difference between this and the initial temperature is the "rise of temperature." Then clean and dry the beaker, and repeat the experiment with 50 grams (50 c.c.) of water in place of the oil. If 50 grams was the amount of the sample taken, then the Maumené Specific Temperature Reaction is obtained by dividing the "rise" obtained with the oil by the "rise" obtained with water and multiply the result by 100. If only 25 grams was the amount of the sample taken and 25 grams of kerosene were added, then a separate extra experiment must be made as follows: take 50 grams of kerosene and determine the rise obtained when 10 c.c. of the concentrated acid are added to it. The Maumené Specific Temperature Reaction of the 25-gram sample is then obtained by subtracting one-half of the rise *obtained with kerosene alone* from the rise obtained with the oil sample, multiplying the remainder by 2, dividing this product by the rise obtained with water, and finally multiplying by 100.

In explanation of this test, it should be pointed out that this reaction of $H_2SO_4$ with the acid molecules at the points of unsaturation is evidently one that evolves heat, and the amount of this "heat effect" is, as always, proportional to the amount of reaction product. Since with different pieces of apparatus the same amount of heat (in calories) will raise the temperature of the whole through a different "rise" of temperature, it becomes necessary to determine the amount of rise with a certain amount of heat. For this purpose the determination with water is made, and by dividing the *rise* with water into the *rise* with oil, the results of the determinations are made independent of the apparatus (also independent of the concentration of the sulphuric acid used).

**14. Demonstration of the Drying of Linseed Oil (Painter's Drying Test).**

Secure three small pieces of glass and spread on them with a glass rod as thin a film of oil as possible: use (1) raw linseed oil, (2) boiled linseed oil, and (3) cotton seed oil. Place the slabs in a *nearly vertical* position in your desk. Note the time in days in which the film attains such hardness that the finger does not stick to it when it is touched.

**15. Illustrations of the Methods Used in Examining and Distinguishing Between Linseed Oil and Similar Oils.**

Linseed oil in paints is frequently adulterated with, or replaced by, corn oil, cotton seed oil, fish oil, soya bean oil, and rosin oil. The following are some of the most important means used by chemists to distinguish between these oils or to ascertain if they are essentially pure. These methods are mainly quantitative, since qualitative tests are of little value due to the fact that they do not reveal the extent of the adulteration. Slight amounts of adulteration are often negligible, and hence only the quantitative test is of value. The principal tests are (a) Iodine absorption number, (b) Maumené specific temperature reaction, (c) specific gravity, and (d) some qualitative tests such as color and odor tests.

(a) Linseed oil is the glycerine ester of several unsaturated acids. Every unsaturated compound has the property of adding on either hydrogen or one of the halogens, such as iodine. If to a given weight of oil an iodine solution is added in excess, a part of the iodine will be absorbed, according to the extent of the unsaturation of the acid or to the extent that an unsaturated acid is present. Then the weight of iodine absorbed in grams × 100 divided by the weight of oil sample in grams is the *iodine number*. This determination requires a good deal of attention in details and technique, and hence will not be made in the laboratory, but the iodine numbers are given for reference in the next article.

(b) The Maumené specific temperature reaction has been described in Art. 13 and the values for different oils are given in the table of the next article.

(c) The *specific gravity* of an oil is the ratio of the weight of a given volume of oil to the weight of an equal volume of water at the same temperature.

Secure a sample of three oils—e. g., of raw linseed oil, of cotton seed oil, and of rosin oil. If desirable the oil from some mixed paint may also be examined: for this purpose allow the paint to settle in a narrow, tall vessel and drain or siphon off some of the supernatant clear oil. If the paint will not settle readily, dilute some of the oil with carbon tetrachloride, and after separating the clear liquid from the solid, remove the carbon tetrachloride by distillation (save it).

Take the specific gravity of these oil samples and determine their Maumené numbers as in Art. 13. By means of these data, decide whether or not the oils are pure.

(d) The *odor* of fish oil is quite distinctive and is used in distinguishing it from linseed oil, since the constants for fish oil closely approximate those of linseed oil. Fish oil should be absent from paints, as it is very undesirable in its drying properties. The following qualitative test is added in order to aid in its detection:

Heat a little of the oil nearly to 100° C. and rub in on the back of the hand: a pronounced fishy odor reveals the presence of fish oil.

(e) A production of *color* reveals the presence of rosin oil.

Rosin oil is another very undesirable, but frequently used, adulterant of linseed oil: surfaces painted with it become "tacky," or "alligator," as it is called, and under the influence of light and air the oil is soon completely destroyed. The quantitative constants given above serve to reveal any extensive adulteration of linseed oil by means of rosin oil, but since it is not always convenient to make such a test the following qualitative test is here added for practical purposes:

Warm a little of the oil and add an equal volume of glacial acetic acid. Mix thoroughly and cool the mixture by means of tap water; then

add one drop of concentrated sulphuric acid: pure linseed oil gives a sea green color, but when adulterated with rosin oil a violet color shows itself temporarily.

**16. The Constants of Some Oils.**

The following table of constants serve to distinguish the various commercial oils. In cases where these constants do not differentiate, it becomes necessary to employ other tests, partially mentioned in Art. 15:

| Name of Oil | Specific Gravity at 15° C. | Maumene Number | Spec. Temp. Reaction | Iodine Number |
|---|---|---|---|---|
| Linseed oil (raw) | 0.931-0.937 | 103-130° | 313-350 | 170-200 |
| Linseed oil (boiled) | 0.936-0.938 | 98-100° | 242-248 | 160-175 |
| China wood oil | 0.938-0.946 | 120-128° | 327-330 | 163-178 |
| Fish oil | 0.927-0.933 | 123-128° | 290-330 | 148-180 |
| Soya bean oil | 0.923-0.924 | 88- 92° | 229-240 | 127-136 |
| Cotton seed oil | 0.921-0.930 | 70- 90° | 163-170 | 101-117 |
| Corn oil | 0.921-0.927 | 70- 90° | 163-170 | 111-125 |
| Rosin oil | 0.987-1.000 | 30- 32° | 80- 83 | 40- 65 |

An inspection of the above table will reveal that linseed oil, fish oil, and China wood (Tung) oil can be classed together as *drying* oils, Soya bean and cotton seed oil as *semi-drying,* and corn and rosin as *non-drying oils.*

**17. Carbohydrates: Their Mutual Relations and Properties.**

The carbohydrates are straight-chain compounds of carbon, hydrogen, and oxygen *only,* in which the hydrogen and oxygen are present in just the ratio to form *water;* hence the name.

Their proximate constituent, into which they may be all resolved more or less directly or readily—is a six-carbon group ($C_6H_{10}O_5$). With reference to this constituent, carbohydrates are thus classified:

(a) *Monosaccharides or glucose,* $C_6H_{12}O_6$; i. e., $C_6H_{10}O_5+H_2O$. Of these, grape sugar and fruit sugar are familiar examples. Five of the carbons have alcohol groupings, and the sixth—an end group—has an aldehyde grouping. Glucoses are usually found in commerce in the form of syrups, because they do not crystallize readily. Their sweetness is only three-fifths of that of cane sugar.

(b) *Disaccharides or saccharoses,* $C_{12}H_{22}O_{11}$; i. e., $2C_6H_{10}O_5+H_2O$. Of these, cane sugar and milk sugar are familiar examples.

(c) *Polysaccharides* $(C_6H_{10}O_5)n$. This group includes (1) starches and (2) cellulose, or woody fibers.

**18. The Change of Poly- and Disaccharides Into Monosaccharides.**

In hot acidified solutions, the members of groups (c) and (b) all change to glucose or monosaccharides. This change is under-

gone quite readily by cane sugar, slowly by starch, and *very slowly* by cellulose. In neutral solutions, all of these substances hydrolyze much more slowly, except at the high temperatures attained under pressure in closed vessels, and which temperature elevation naturally accelerates the change. In alkaline solutions hydrolysis does not take place to any notable extent. On the whole, the carbohydrates may be said to be very resistant to dilute alkaline solutions, but they react readily with dilute acids.

To recognize carbohydrates they are "hydrolyzed" to glucose by boiling them in an acidified solution, and then the glucose is tested for by means of *Fehling's* solution. This test depends upon the reduction of cupric salts to cuprous salts, while the aldehyde group on glucose is oxidized. Cane sugar and starch, etc., themselves do not react with Fehling's solution.

The sensitiveness of the Fehling's test is due to the fact that monosaccharides have an aldehyde grouping on the end carbon, which is lacking in their higher members. When an alkaline solution of cupric tartrate is added to an aldehyde, the aldehyde becomes oxidized to an acid, while the cupric salt is reduced to the cuprous state, the red color of the cupric oxide being the color test desired.

**19. The Hydrolysis of Cane Sugar, Starch and Cellulose.**

Make the Fehling's test on a solution of (a) glucose, (b) cane sugar, (c) starch which has been "dissolved" by stirring a little starch into some cold water and then heating the mixture.

To make the test, mix 1 c.c. of copper sulphate solution with 1 c.c. of a solution containing sodium potassium tartrate and caustic soda, using enough of the second solution to dissolve the precipitate of cupric hydroxide first formed: heat this mixture to boiling and add a few drops of the solution to be tested. If monosaccharides are present, a brick-red precipitate will be obtained.

Next "hydrolyze" some cane sugar: dissolve a little sugar in water, add a few drops of dilute sulphuric acid, and boil the solution for one to three minutes. Neutralize the acid with sodium hydroxide and test the solution with Fehling's solution! "Hydrolyze" some starch by acidifying the starch solution (?) prepared above and boiling it. It will be necessary to continue the boiling for ten to twenty minutes, because starch hydrolyzes more slowly than cane sugar. Test the solution with Fehling's solution.

Filter paper or cotton are examples of pure cellulose. Try to hydrolyze a sample of cellulose by keeping it in acidified water at 100 degrees: this may be done by placing the container (i. e., a test tube or a flask) in a beaker or other vessel in which water is boiled. After the water in the container is hot, the container may be stoppered to prevent the evaporation of the water in it. After treating the cellulose for the rest of the laboratory period, set it aside until the next laboratory period, then boil again for about two hours. Then test the solution with Fehling's solution.

**20. The Hydrolysis of Poly- and Disaccharides to Monosaccharides by Means of Living Organisms.**

These *hydrolytic* changes of starch or cellulose do not consist of one step only, but of several, and if the change is arrested

at different points different intermediate products may be obtained. Thus starch, which is insoluble, may be changed to an intermediate soluble compound, dextrine, which is not yet a monosaccharine because it does not respond to the Fehling's test. Similarly, cellulose may be hydrolyzed to intermediate compounds. Of course, when in either case the action is continued long enough, the substance is finally converted to a monosaccharide.

The hydrolysis of starch and of sugar (but not of cellulose, to any practical extent) is also brought about by the action of *enzymes.*

These enzymes may be produced (a) by micro-organisms, such as yeasts and bacteria; (b) by sprouting seeds, etc., e. g., diastase is formed by sprouting barley and hydrolyzes starch to a disaccharide; (c) by special processes of secretion in the higher animals, e. g., ptyalin in saliva.

For the sake of accuracy it should be mentioned that only the monosaccharides are directly "fermentable" into alcohol and carbon dioxide. The action of yeast upon disaccharides is noticeably made up of *two* consecutive actions due to distinct enzymes which are both produced by the yeast plant:

(1) *The hydrolysis of the disaccharides.*

(2) *The change of monosaccharide to alcohol and carbon dioxide.*

In sugar houses the presence of yeast germs must be carefully guarded against by cleanliness. A "sour mill," as it is called, is easily obtained through the fact that the alcoholic fermentation of sugar may be followed immediately by the acetic acid fermentation of the alcohol, because the vegetable organisms which produce these fermentations are frequently carried about by the air. Acetic acid, just as other acids, catalyzes the hydrolysis of disaccharides to monosaccharides. The latter do not "crystallize out" ordinarily as the solutions are concentrated, and by making solutions more viscous they interfere with the crystallizing out of the cane sugar.

NOTE.—This effect of the glucose is made use of in making "pulling candy": the sugar solution is acidified with vinegar and boiled. Thus, as part of the cane sugar is hydrolyzed, a syrup of non-crystallizing glucose is produced out of which even the cane sugar present does not crystallize readily.

**21. Effect of Ptyalin Upon the Solubility of Starch.**

Make a thick starch paste by mixing a teaspoonful of powdered starch in half a beaker of cold water and then boil for three or four minutes. Cool the starch paste to body temperature and divide it into two portions. To one portion add half a test-tube full of saliva. Pour each portion on dry filter papers in two separate funnels, and stand them aside

for an hour, collecting the filtrates. Observe that the one to which saliva was added gives the larger amount of filtrate, showing that saliva has made the starch soluble. Test the filtrate for sugar by Fehling's test. The increase in solubility is due to the conversion of starch into dextrine and glucose.

### 22. The Manufacture of Sugar.

Sugar is obtained from cane by pressing out the juice between rollers, and from beets by "soaking" the sliced beets in water. In either case the liquid contains also some albuminous matter which would ferment readily; it is removed by boiling the solution to coagulate the albumen. A small amount of free acids present is neutralized with lime water, and precipitated, because the calcium salts formed are insoluble. The liquid, after being freed from the solids, is evaporated to crystallize the sugar.

### 23. The Manufacture of Starch.

The separation of starch out of corn, potatoes, rice, wheat, etc., requires not only the softening (soaking) and crushing of the grain, but also the separation of the starch from other matter—usually proteins. (See below.) Some of these are insoluble—for instance, the gluten in wheat—while others are soluble. Besides proteins, oils are present—particularly in the seed germs. The separation of these substances is essentially a mechanical one and consists mainly of extensive kneading of the mass and washing it with a stream of water: the suspended matter usually settles so that the starch forms a separate layer.

To illustrate the above, make a paste of wheat flour and place it in a small cloth bag. Then knead this bag and contents while holding it in a vessel filled with water to collect starch. Finally, to remove the starch as thoroughly as possible from the contents of the bag, continue to knead it under a stream of tap water until no more starch is obtained.

Test the starch with a drop of aqueous iodine (and KI) solution: the deep blue color obtained is characteristic of starch. Test the starch with Fehling's solution to ascertain if glucose is present.

Test the starch water qualitatively for protein. (See below.)

Test the contents of the bag for (a) starch; (b) protein (gluten).

### 24. The Chemical Properties of Cellulose.

As is indicated in the foregoing, cellulose is particularly resistant to the action of reagents in dilute solutions. This is well illustrated by the fact that cotton and linen goods in cleaning are boiled even in strong soap solutions. Cellulose resists the oxidizing action of chlorine even; hence cotton and linen goods are bleached by means of hypochlorite solutions.

However, cellulose is readily attacked and disintegrated by vapors of acids; or if, after being steeped in dilute acids, it is

allowed to dry with the acid on it. In these respects—that is, in its behavior with alkalies, with chlorine, and with acids,—it presents a striking contrast to wool, which is readily attacked by alkalies, so that it cannot even be boiled in soap solutions; it is destroyed by chlorine, hence must be bleached by other means (hydrogren peroxide, sulphur dioxide), but it resists acids even when they are evaporated on its surface.

**25. The Extraction of Cellulose From Plants and Its Preparation for Paper Making.**

Although the *woody* or fibrous parts of plants are composed in the main of cellulose, yet they also contain other substances of albuminous, starchy or resinous nature, which are intimately mixed with the cellulose and frequently serve to bind the cellulose fibers together.

Cellulose exists in plants in many different states of hydration. In the green, growing parts, it is largely present in a more hydrated form than that which corresponds to the formula $(C_6H_{10}O_5)$, while wood contains a great deal in a form less hydrated than that which corresponds to this formula (lignocellulose). The hydrated forms of the green parts of plants are more or less easily attacked by the digestive enzymes and converted to soluble material (digested!) while cellulose and the lignocellulose are practically not attacked. However, they aid mechanically in the digestion of other components of food.

Pure cellulose may be prepared from plant material as follows: plant material is freed from the hydrated cellulose, from starch and from some of the protein matter by boiling it with dilute acids (1 per cent sulphuric acid or 10 drops of concentrated sulphuric acid to every 100 c.c. of water); then the residue is washed with hot water to remove the acid, and it is boiled in a very dilute sodium hydroxide solution (about 1 c.c. of 20 per cent solution to every 100 c.c. of water): this will remove resins, oily matter, and the remaining protein matter. The residue is washed again with hot water, and finally the last traces of foreign matter—some of which color the material—are removed by oxidation (bleaching!) with chlorine: for this purpose the cellulose is steeped in a small amount of dilute hydrochloric acid to which a very small amount of potassium chlorate has been added. This mixture is heated in a water bath for a few minutes, and afterwards the acid is removed *thoroughly* by washing first with water, and then with a very dilute solution of soda. The residue may be dried on a clock glass placed on top of a beaker half full of boiling water.

In the analysis of foods and feedstuffs an amount of 1 to 5 grams of the material is weighed, and treated as above stated, to remove the other materials from the cellulose.

In the commercial preparation of cellulose from wood—i. e., for paper—the treatment is usually not nearly as thorough. For the cheapest grades of wrapping paper the fibers are simply torn apart by "grinding" the wood on a grindstone (mechanical pulp!). But

for better grades of paper the foreign matter, which glues the fibers together, must be dissolved out by chemical treatment. Only one kind of solution is used in any case.

In most cases this is a solution of bisulphite of calcium and of magnesium. These salts are cheap and very effective. A solution of sodium carbonate, or a solution of sodium sulphate with a little sodium hydroxide are used in some plants. In all cases the boiling takes place in closed vessels under pressure,—hence at as high a temperature as possible so that the chemical actions may go on as rapidly as possible. The wood is put into the boiler in the form of chips.

### 26. Organic Compounds Which Contain Nitrogen.

None of the organic compounds considered so far contain nitrogen, yet the organic compounds which contain nitrogen are not only large in number, but they are very important, and a certain amount of them in the food of animals and plants is absolutely necessary for their sustenance. The nitrogen compounds in animal and vegetable bodies appear to be derived from ammonia by substitution of one or more of its three H's by carbon groups. According to the basic or acidic nature of the carbon radical, the resulting compound will be more basic or less basic than ammonia, and hence its tendency to salt formation (by addition with an acid, e. g., $NH_3$, HCl) is either greater or less than that of ammonia. The hydrocarbon radicals of the paraffin series ($CH_3$, $C_2H_5$, $C_3H_7$, etc.) are all strongly basic, and hence their nitrogen compounds are more basic than ammonia (e. g., $CH_3NH_2$, $C_2H_5NH_2$, $(CH_3)_3N$). They are called "amines" and they form salts like this: $CH_3NH_2$,HCl called methyl amine hydrochloride. When the "N" is connected to the carboxyl group, which is acidic in character, the compounds are only faintly basic, e. g., $HCO.NH_2$ which is derived from formic acid HCO.OH and is called "formamide." Among the important nitrogen compounds found in animal bodies is urea, $OC(NH_2)_2$, which is sufficiently basic to form a fairly stable salt, $OC(NH_2)_2$ HCl, urea hydrochloride. In the vegetable bodies the alkaloids, nicotine, quinine, etc., are the best known nitrogen compounds. They form stable salts with acids.

### 27. Proteins.

Most of the plant and animal tissues which contain nitrogen are classed together as *proteins*. Proteins also contain sulphur. The per cents of the different elements in protein compounds from various sources range as follows:

Carbon, 51.2 to 54.7 per cent.
Hydrogen, 6.7 to 7.6 per cent.

Nitrogen, 15.2 to 18 per cent.
Oxygen, 20.2 to 23.5 per cent.
Sulphur, 0.3 to 2 per cent.

There is no marked distinction in chemical composition between proteins of plant and of animal origin; yet they frequently have different properties, and they cannot in general be substituted, weight for weight, one for the other in food rations, because they are not equally digestible, and, even after digestion, they do not serve equally to replace or build up animal tissues.

Proteins, like carbohydrates, are insoluble in ether, carbon tetrachloride and other special solvents for fats; hence fats may be readily separated from animal and vegetable tissues without disturbing the other components.

The many different proteins which have been recognized and which have been given special names may be classified as follows:

(a) *Simple proteins,* e. g., albumen, or egg white, gluten in wheat, etc.

(b) *Compound or conjugated proteins,* i. e., combinations of simple protein molecules with molecules of other substances, e. g., casein of milk, which is a phospho-protein.

(c) *Derived proteins,* which correspond to hydrolyzed products of simple proteins; and they are obtainable from either (a) or (b), e. g., peptones, the products formed by the action of pepsin on proteins.

The different proteins differ largely in solubility. Only a few are soluble in water without change (e. g., albumen, a simple proteid, is soluble in water; globulin, also a simple proteid, is soluble in a dilute salt solution). These soluble proteins are changed to a coagulated form at higher temperatures (above 65-75 degrees C.); hence they are precipitated when their solutions are boiled. The chemical change produced by this boiling is a slight hydrolysis. Most proteins are soluble in either dilute acids or dilute alkalies, or in both, which dissolution is accompanied by a hydrolytic change in the substance.

If the hydrolytic action is continued, the proteins are finally broken up into soluble substances. For instance, the very insoluble protein called *keratine,* which is the main component of nails, hair, hoofs, horns, etc., may be hydrolyzed into gelatine by boiling water. Gelatine is insoluble in cold water, but soluble in hot water. By long-continued boiling, gelatine finally is hydrolyzed into simpler substances which are soluble in both hot and cold water.

### 28. The Hydrolysis of Proteins by Means of Enzymes.

This hydrolytic change of proteids, which can be brought about by acids, alkalies and by hot water is also brought about by enzymes, just as with carbohydrates.

To illustrate: Dissolve a little egg albumen in half a test-tube full of water, boil the solution to coagulate the albumen, cool it, add to it about 10 to 15 drops of neutral pepsin solution, then add 3 to 4 drops of dilute hydrochloric acid, shake the mixture and place the test-tube in an air bath at a temperature of 38 degrees C.—not higher. Note that the coagulum is gradually dissolved (digested).

*Pepsin* is the enzyme found in the gastric juice which, in the presence of hydrochloric acid, hydrolyzes protein into soluble forms so that they may pass through the walls of the digestive tract into the circulatory system.

### 29. The Xanthoproteic Test for Proteins.

Secure a little egg albumen dissolved in water, add a few drops of concentrated nitric acid, and boil the mixture for a minute or two. Then add a few drops of ammonia to neutralize all of the acid: the yellow color first produced by the nitric acid will change to an orange color on the addition of the ammonia, and this color effect is indicative of the presence of proteins.

### 30. The Food Value of the Different Food Constituents.

Protein matter is a necessary ingredient of the foods for all animals because their body tissues are composed mainly of protein matter and the broken down body tissues are replaced, for the most part, more or less directly from the protein matter in the food.

The ratio of the digestible non-nitrogenous food ingredients to the digestible protein matter in foods is called the *nutritive ratio*. For the proper feeding of men and animals, the meals should be so designed that the nutritive ratios of all the foodstuffs together have certain values. Thus, for a man with moderate physical exercise the ratio should be about 5.8; for a man with a hard muscular exercise, this ratio should be 6.5; and for one with little exercise, the ratio should be 5.5. These figures have been obtained by the analysis of foods with which men have done well under these conditions. However, men can exist and do fairly well with considerably lesser relative amounts of protein matter in their food. Most meals contain larger ratios of protein matter: the extra amount of protein matter serves merely to give heat—just as an equal amount of a carbohydrate would do.

Aside from the requirement of a certain minimum amount of protein matter in foods, the main requirement that foods must fulfill is that they furnish a certain amount of fuel for the main-

tenance of the temperature of the body. The fuel value of foodstuffs may be calculated by means of Ruebner's factors. These are:

1 pound of protein or of carbohydrates gives 1860 calories;
1 pound of any animal or vegetable fat gives 4220 calories.

This means that these substances, when burned to water and carbon dioxide, evolve this much heat. It is possible to estimate the fuel value of foods from these figures because the digested—assimilated—portions of food are converted almost entirely to water and carbon dioxide.

The fuel value of a food may be said to be the most direct measure of its value.

Ascertain the analysis of any particular foodstuff—say, of oatmeal—and calculate its fuel value.

Since the quantity of food a man wishes to eat at a meal is generally judged by its bulk or volume, it becomes advisable to choose foods in different seasons or climates so that *roughly equal* volumes have greater or lesser fuel values as the weather, climate, or the occupation of the individual may require.

The daily rations of men have been given by one authority (Atwater) to be such as to have the following fuel values:

For a woman with light muscular exercise, 2800 calories.
For a woman with moderate muscular exercise, 3500 calories.
For a man with light muscular exercise, 4060 calories.
For a man with hard muscular exercise, 5700 calories.

### 31. The Composition of Food and Feed Stuffs.

Foods and feedstuffs are ordinarily considered as made up of the following six "proximate" components: water, ash, fats, carbohydrates, protein, and crude fiber. In Texas every bag of feedstuff must be tagged with a label which states the per cents of these components present in the contents, as determined by the State Chemist, at College Station. The analysis of a foodstuff should report the same constituents.

Vegetable foods furnish some protein. Wheat has a larger per cent of protein than any other cereal. It contains from 10 to 18 per cent of protein (gluten) and from 65 to 70 per cent of carbohydrates exclusive of fiber. Animal foods, with the exception of milk, furnish practically no carbohydrates. Milk furnishes all essential food constituents. Since this substance is such a frequently used article of diet, a demonstration of its components is desirable.

### 32. The Components of Milk.

Determine the specific gravity of milk: that of fresh milk is between 1.029 and 1.034, while that of skimmed milk is higher.

Determine the amount of butter fat present, by Babcock's method: Pipette off 17.6 c.c. of the carefully mixed sample into a test bottle and add 17.5 c.c. of commercial sulphuric acid. Mix, and when the curd is dissolved, whirl the test bottles in the centrifuge for four minutes at the required speed for the machine used. Add boiling hot water, filling to the neck of the bottle, and whirl for one minute; again add boiling water so as to bring the fat within the scale on the neck of the bottles, and after whirling for one minute more read the length of the fat column. These readings must be made at a temperature between 30 and 50 degrees F., when the fat is wholly liquid. The readings give the per cent of fat in the milk direct.

In Texas milk must have at least 3.5 per cent of butter fat to be considered unadulterated.

*Caseinogen* is the chief proteid of milk. To separate it from the liquid, saturate 50 c.c. of milk with some neutral salt, such as sodium chloride or magnesium sulphate. The caseinogen and the fats will be precipitated together. Filter, saving both precipitate and filtrate.

Dissolve the precipitate in clear lime water or in a very dilute sodium hydroxide solution. Heat the solution so that the fats will melt and float on top, and then neutralize the alkali cautiously with acetic acid: the protein will be precipitated again.

Milk also contains *albumen*. This will be found in the filtrate obtained above. Heat this to precipitate the albumen. This is the substance that forms the *skin* when milk is boiled.

Finally, demonstrate the presence of milk sugar by testing the same liquid with Fehling's solution.

### 33. Some Chemical Properties of Fibers: Cotton, Wool, Silk.

The properties of cotton (cellulose) and of wool (protein: keratine) have been given above. Silk is a nitrogenous animal fiber with properties somewhat different from those of wool. It contains no sulphur. It is not quite as easily attacked by alkalies or by chlorine as wool, but it will dissolve in strong caustic alkali solutions as wool does. Dilute acids do not affect it as they affect cellulose. True silk may be readily distinguished from artificial silk, because the latter is merely cellulose in composition and properties.

The simplest way to distinguish between cotton on one hand and silk and wool on the other is to try to burn the material: if it burns readily after ignition, and gives out no particular odor, and leaves a white ash, it is cotton. Silk and wool do not continue to burn readily after ignition: the burning of wool produces a decided odor similar to the familiar odor of burned feathers, the burning of silk produces a similar, but fainter odor, and these animal fibers leave a crisp coal. Confirm these facts by burning samples of the fibers.

Woolen fibers can be recognized under the microscope by the scales of their surfaces. Silk and cotton fibers have smooth surfaces. The cotton fiber appears as being very much twisted. Samples of the different fibers should be examined under a microscope.

Secure samples, of about one gram each, of white silk, white wool, and white cotton (yarn or cloth). Place these samples in small beakers, cover them with a ten per cent solution of sodium hydroxide, and stir the mixture so that the solution may act thoroughly on the fibers: the cotton will remain undissolved, but the silk and the wool will dissolve. To the solutions of the latter, add a little lead acetate: the wool solution will give a precipitate of lead sulphide, but the silk solution should give none.

Secure a piece of cloth composed of both wool and cotton, and dissolve out the wool by means of a ten per cent solution of sodium hydroxide.

Silk can be separated from wool and cotton by means of a solution of zinc chloride which is so concentrated that it has a specific gravity of 1.70, and in which some zinc oxide has also been dissolved.

Wool must frequently be freed from burs and from seeds, or even from cotton: for this purpose, it is steeped in dilute hydrochloric acid, or in dilute sulphuric acid, and then allowed to dry partly. On drying, the dilute acid attacks and disintegrates the cellulose (cotton, burs, etc.), but does not affect either wool or silk appreciably.

For a demonstration, secure a bit of cotton cloth, steep it in some dilute hydrochloric acid, squeeze out the excess of acid and lay the cloth aside to dry: when dry, it will be found to easily disintegrate mechanically.

### Questions on Chapter XIV.

1. Draw one structural possibility for oleic acid, linoleic acid and linoleinic acid. Draw the structural formula, large scale, of one molecule of olein, one molecule of palmitin, and one molecule of stearin. Calculate how many grams of olein will react with one gram of iodine. Calculate how many grams stearin will react with one gram of sodium hydroxide. In each case begin your calculation by stating the chemical reaction which takes place. Explain how stearin is made from cotton seed oil: does it need to be kept cold in order to keep it in the solid form after its extraction?

2. Describe how you would extract the oil from any food material such as corn kernels. How is cotton seed oil refined? Explain why the conversion of a part of the oil into soap serves to remove the impurities from the oil (what is the nature of the impurity?) and why does the refined oil keep better than the raw oil? Describe how to determine the pure soap material (its amount) in a commercial soap. Why may soap be used to measure the amount of "hardness" in potable waters: state all you know concerning the nature or cause of hardness in water and how soap reacts with the substances in hard water.

3. Why is the Maumené Test a logical means of examining oil to be used for paints? What is the action of a "japan" in paints? How is linoleum or oil cloth or printers' ink produced?

Why does hard oil dry so much more rapidly than unboiled linseed oil? What is the composition of linseed oil?

4. Starch, sugar and digestible cellulose are all considered to be of equal value as a food material: explain why it is logical to consider them thus. How is paper made? How is sugar manufactured? State exactly what is meant by the statement that all digestive changes which foodstuffs undergo are hydrolytic changes (this applies only to carbohydrates and to proteins).

5. What six items does the Texas State Feed Law require to be known and placed on the label of feedstuffs? Wherein do proteins differ from all other foodstuffs? Why are proteins necessary ingredients of foods? What is the nutritive ratio? Is there a hard and fast mathematical rule concerning the fraction of protein in all foods for man or is considerable variation in the amount of protein permissible? As long as a sufficient amount of protein is provided for, then only one other function is to be performed by food in the body: that is, to furnish the energy to keep the organisms going: the amount of energy which a food can give can be measured in a convenient way. What is this way? State Ruebner's factors. State what you know concerning the composition of milk and flour.

6. State what you know concerning the composition and chief chemical properties of cotton, wool, and silk.

# APPENDIX

## INTERNATIONAL ATOMIC WEIGHTS, 1918

| | Symbol | Atomic Weight | | Symbol | Atomic Weight |
|---|---|---|---|---|---|
| Aluminium | Al | 27.1 | Molybdenum | Mo | 96.0 |
| Antimony | Sb | 120.2 | Neodymium | Nd | 144.3 |
| Argon | A | 39.88 | Neon | Ne | 20.2 |
| Arsenic | As | 74.96 | Nickel | Ni | 58.68 |
| Barium | Ba | 137.37 | Niton | Nt | 222.4 |
| Bismuth | Bi | 208.0 | Nitrogen | N | 14.01 |
| Boron | B | 11.0 | Osmium | Os | 190.9 |
| Bromine | Br | 79.92 | Oxygen | O | 16.00 |
| Cadmium | Cd | 112.40 | Palladium | Pd | 106.7 |
| Caesium | Cs | 132.81 | Phosphorus | P | 31.04 |
| Calcium | Ca | 40.07 | Platinum | Pt | 195.2 |
| Carbon | C | 12.005 | Potassium | K | 39.10 |
| Cerium | Ce | 140.25 | Praseodymium | Pr | 140.9 |
| Chlorine | Cl | 35.46 | Radium | Ra | 226.0 |
| Chromium | Cr | 52.0 | Rhodium | Rh | 102.9 |
| Cobalt | Co | 58.97 | Rubidium | Rb | 85.45 |
| Columbium | Cb | 93.1 | Ruthenium | Ru | 101.7 |
| Copper | Cu | 63.57 | Samarium | Sa | 150.4 |
| Dysprosium | Dy | 162.5 | Scandium | Sc | 44.1 |
| Erbium | Er | 167.7 | Selenium | Se | 79.2 |
| Europium | Eu | 152.0 | Silicon | Si | 28.3 |
| Fluorine | F | 19.0 | Silver | Ag | 107.88 |
| Gadolinium | Gd | 157.3 | Sodium | Na | 23.00 |
| Gallium | Ga | 69.9 | Strontium | Sr | 87.63 |
| Germanium | Ge | 72.5 | Sulphur | S | 32.06 |
| Glucinum | Gl | 9.1 | Tantalum | Ta | 181.5 |
| Gold | Au | 197.2 | Tellurium | Te | 127.5 |
| Helium | He | 4.00 | Terbium | Tb | 159.2 |
| Holmium | Ho | 163.5 | Thallium | Tl | 204.0 |
| Hydrogen | H | 1.008 | Thorium | Th | 232.4 |
| Indium | In | 114.8 | Thulium | Tm | 168.5 |
| Iodine | I | 126.92 | Tin | Sn | 118.7 |
| Iridium | Ir | 193.1 | Titanium | Ti | 48.1 |
| Iron | Fe | 55.84 | Tungsten | W | 184.0 |
| Krypton | Kr | 82.92 | Uranium | U | 238.2 |
| Lanthanum | La | 139.0 | Vanadium | V | 51.0 |
| Lead | Pb | 207.20 | Xenon | Xe | 130.2 |
| Lithium | Li | 6.94 | Ytterbium | Yb | 173.5 |
| Lutecium | Lu | 175.0 | Yttrium | Yt | 88.7 |
| Magnesium | Mg | 24.32 | Zinc | Zn | 65.37 |
| Manganese | Mn | 54.93 | Zirconium | Zr | 90.6 |
| Mercury | Hg | 200.6 | | | |

VAPOR PRESSURES OF WATER

| Temperature | | Pressure in mm. of Hg | Temperature | | Pressure in mm. of Hg |
|---|---|---|---|---|---|
| Centigrade | Fahrenheit | | Centigrade | Fahrenheit | |
| 0° | 32.0 | 4.60 | 24° | 75.2 | 22.18 |
| 5 | 41.0 | 6.53 | 25 | 77.0 | 23.55 |
| 8 | 46.4 | 8.01 | 26 | 78.8 | 24.99 |
| 10 | 50.0 | 9.16 | 27 | 80.6 | 26.50 |
| 12 | 53.6 | 10.46 | 28 | 82.4 | 28.10 |
| 14 | 57.4 | 11.91 | 29 | 84.2 | 29.78 |
| 15 | 59.0 | 12.70 | 30 | 86.0 | 31.55 |
| 16 | 60.8 | 13.53 | 35 | 95.0 | 41.83 |
| 17 | 62.6 | 14.42 | 40 | 104.0 | 54.90 |
| 18 | 64.4 | 15.36 | 50 | 122.1 | 91.98 |
| 19 | 66.2 | 16.35 | 60 | 140.0 | 148.79 |
| 20 | 68.0 | 17.39 | 70 | 158.0 | 233.09 |
| 21 | 69.8 | 18.49 | 80 | 176.0 | 354.64 |
| 22 | 71.6 | 19.66 | 90 | 194.0 | 525.45 |
| 23 | 73.4 | 20.89 | 100 | 212.0 | 760.00 |

THE METRIC SYSTEM AND EQUIVALENTS

I. *Length:* (a) 10 millimeters=1 centimeter
10 centimeters=1 decimeter
10 decimeters =1 meter
1000 meters =1 kilometer

(b) 1 meter =1.094 yds.=3.286 ft.=39.37 in.
1 kilometer =0.6214 miles

II. *Volume:* (a) 1000 cubic centimeters=1 liter.

(b) 1 liter=61.03 cu. in.=1.057 quart (U. S).
1 cu ft.=28.32 liters.

III. *Weight:* (a) 10 milligrams=1 centigram
10 centigrams=1 decigram
10 decigrams =1 gram
1000 grams =1 kilogram

(b) 1 kilogram =2.205 lbs. av.
1 lb. av. =453.6 grams.
1 oz. av. = 28.35 grams

### RELATIONS OF TEMPERATURE SCALES

The ordinary domestic and the engineer's scale of temperature is the Fahrenheit scale, upon which the freezing-point of pure water is 32° F. and the boiling-point under atmospheric pressure is 212° F.—an interval of 180°. The scientific scale is the Centigrade (or Celsius) scale, upon which the freezing-point of pure water is 0° C. and the boiling-point 100° C.—an interval of 100°.

The degree Centigrade, therefore, is $\frac{180}{100}$ or 9/5 of 1° Fahrenheit; the degree Fahrenheit is $\frac{100}{180}$ or 5/9 of 1° C. The following conversion formulæ are useful for quickly converting temperatures from one scale to the other:

$$C°=5/9\ (F°-32);\ F°=9/5\ (C°)+32.$$

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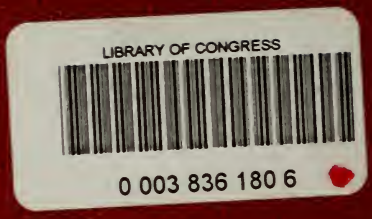
L6Fe20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